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A TEXT-BOOK

OF

GENERAL DESCRIPTIVE CHEMISTRY

(INORGANIC.)

BY

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PREFACE.

In compiling the descriptive portions of this work, I have chiefly used Graham-Otto's *Lehrbuch der Allgemeinen Chemie* (last edition) and Ladenburg's *Handwörterbuch der Chemie*, although, wherever any of the facts which it was necessary to incorporate seemed doubtful, I have consulted the original sources in the chemical periodicals; of course, the discoveries which have been brought forth in the last few years, I have taken entirely from the latter. In the discussion of the double halides, of fluosilicic acid and of similarly constituted bodies, I have adopted the views which have recently been brought into prominence by the publications of Prof. Ira Remsen, both in his larger text book and in his contributions to current chemical literature; the same may be said in regard to the polysulphides, although I believe that the structural formulæ assigned to the latter bodies are based upon slight experimental evidence. In my views upon the subject of valence and in the use of structural formulæ, I may, possibly, be regarded as being too conservative by many of my colleagues but I have been led to adopt the views which I hold by the growing conviction that the too dogmatic use of supposed laws of valence and of constitutional formulæ, founded upon very incomplete experimental evidence, is causing more harm than good to the advancement of chemical science. In discussing chemical changes and reactions, I have endeavored not to present the various topics as a series of isolated facts, but as being connected, the one with the other, so that there is scarcely any one of the numerous phenomena which are mentioned in this work which does not find its analogon in some other portion of the field of chemical study. I have attempted, especially, to call attention to the influence exerted by the nature of the elements which make up a chemical compound upon the character of that compound itself, and, in tracing those connections, I may, possibly, have been led somewhat into the realm of speculation, notably so, perhaps, in my endeavor to explain the behavior of the hydrogen compounds of the not-metals by taking into consideration the relative influence exerted by the masses of the atoms which go to make the molecules; I hope, however, that the new arguments I have ventured on during the progress of this work will not be condemned without a hearing. Of course, a very complete knowledge of descriptive chemistry, both inorganic and organic, is necessary before the study of so-called physical chemistry can be pursued with profit, nevertheless, wherever it

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has seemed to me that some elementary facts from the realm of physical chemistry would be comprehended by the pupil taking up beginning chemistry, I have not hesitated to introduce the latter, while, at the same time, giving the references to the best of the smaller text books on the subject. The atomic weights which I have used are taken from the table recently prepared by F. W. Clarke, with the atomic weight of oxygen (taken as the standard) placed at 16.

The laboratory notes in the appendix cover only the ground taken by the not-metals, they are not intended as a laboratory manual, but mainly as a guide to both teacher and pupil in compiling a list of experiments. I believe that every teacher prefers using his own methods for laboratory instruction with, of course, his own selection of the work to be pursued; in my own laboratory I follow a manual which is made up of brief directions accompanied by a very complete set of questions and all of the latter must be answered by the pupils. I do not think, however, that pupils should be left in the laboratory without other than a printed guide; far from it, I like to see the instructor always present in the room during laboratory hours, guiding and assisting his pupils and, not infrequently, working with them.

PAUL C. FREER.

ANN ARBOR, MICH., September, 1892.

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ERRATA.

Page 67, 11th line from below, for Arogadro read Avogadro.

Page 70, 10th line from above, for 70 K read 170 K.

Page 76, 10th line from below, after hydrobromic acid gas, add, from gaseous bromine.

Page 83, 11th line from below, the number 84 K is for the formation of hydrobromic acid from liquid bromine.

Page 94, 9th line from above, for 186 K read 168 K.

Page 190, 11th line from below, for $H N O_3$ read $2 H N O_3$.

A TEXT-BOOK
OF
GENERAL DESCRIPTIVE CHEMISTRY.

GENERAL CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

THE COMPOSITION OF CHEMICAL COMPOUNDS.

A fundamental theory of modern physical science is based on the atomic hypothesis, for by it many changes which take place in nature are explained. The theory that matter is not infinitely divisible, but that upon attempted separation into smaller parts a mass not capable of further subdivision would appear, was held by the Greek and Roman philosophers—by Democritus, Aristotle, Epicurus and Lucretius—and has been transmitted to the present generation with many important modifications. The idea, for we could scarcely dignify by the name of theory that which had so little foundation in experiment, was partially lost sight of during the dark ages of chemistry; during the time of the alchemists when the sole aim of chemical study was mercenary, when scepticism on the one hand and popular superstition on the other had stifled all originality of thought and coördination of theory in this field of knowledge; it suffered no better fate at the hands of those who succeeded the alchemists, for they were men who used their small knowledge of chemical facts for the purpose of discovering new drugs and remedies; it only could expand into what it is, when chemistry freed from the bane of superstition, began to be followed for the sole purpose of increasing human knowledge.

We trace the growth of a science of chemistry from the beginning of the eighteenth century, for then chemists began to have theories founded on experiment, undoubtedly often false and misleading, but nevertheless of such a nature that scientific progress was inevitable from the attempt to answer the problems arising. In this century fell many of the greatest discoveries of modern chemical science; notably the proof of the existence of more than one variety of gas; of the formation of the atmosphere from two kinds of matter, oxygen and nitrogen; that water can be formed by the union of oxygen and hydrogen; while substances in burning absorb a constituent of the atmosphere, and in so doing gain in weight, the gain in weight of the burning substance being exactly equal to the loss in weight sustained by the atmosphere. To the knowledge so gained we owe our understanding of a principle of nature upon which all chemical speculations are based; that of the conservation of matter. The English chemists Black, Priestley and Cavendish were the men whose efforts developed so many new facts; but it was by the clear insight of the Frenchman Lavoisier into the meaning of these discoveries, that a greater service was rendered to humanity in giving a proper explanation of the phenomena involved. Without the discovery of oxygen by Priestley, or of the composition of water by Cavendish, Lavoisier might not have proved the law of the conservation of matter nor have established the theory of combustion held at the present time; but it is equally true that without Lavoisier's genius the work of the English scientists would not have accomplished the result of preparing chemistry for the unprecedented advance recorded of it in the nineteenth century. During the time of these great discoveries the atomic theory, though tacidly accepted, was not made the basis of investigation; but when the present century dawned chemists began to feel the need of some rational explanation of those phenomena which most concerned them.

The first decade brought the discovery that when two subtances unite chemically a compound was always formed in unvarying proportions by weight. Thus iron and sulphur unite to form iron sulphide in which we have for every four parts of sulphur seven parts by weight of iron, no matter where or how the combination takes place; furthermore, there is another compound of iron and sulphur in which for seven parts by weight of iron we have eight of sulphur. Under whatever conditions or in whatever place either of these sulphides are formed, the resulting proportions are always the same. If there is more sulphur present than is necessary for combination, then the excess of sulphur remains unchanged, but if more iron is employed, then iron is found after the union. We have two compounds of carbon and oxygen called oxides, for reasons similar to those which gave the name of sulphides to the compounds of iron and sulphur. In one of these, six parts by weight of carbon are united with eight parts of oxygen, in the other six parts of carbon are united with sixteen parts of oxygen. What was true as regards iron, carbon, oxygen and sulphur characterized the multitude of other substances which were then studied with the object of ascertaining the relative proportions by weight in which the constituent parts were united. To these discoveries was added the demonstration that the relative proportions of sulphur and oxygen, for instance, were preserved in whatever compound they were encountered. Thus sulphur and oxygen form two compounds, called oxides of sulphur, in one of which four parts by weight of sulphur unite with four of oxygen, in the other four of sulphur with six of oxygen. The relationship in the weights of oxygen and sulphur in the various compounds cited becomes apparent if we calculate the weights placing sulphur at 16, while preserving the proportion between the various parts, thus:—

Iron and sulphur...............	28	parts	of	iron	unite	with	16	of	sulphur.
" " "	28	"	"	"	"	"	32	"	"
Carbon and oxygen.............	6	"	"	carbon	"	"	8	"	oxygen.
" " "	6	"	"	"	"	"	16	"	"
Sulphur and oxygen...........	16	"	"	sulphur	"	"	16	"	"
" " "	16	"	"	"	"	"	24	"	"

These relations represent actual facts whatever explanation we may see fit to attach to them; but such facts as these necessarily give rise to speculations as to the underlying causes. Why should it not be possible to have 28 parts of iron united at one time with 16 parts of sulphur, at another with 17 parts, at yet another with 15 parts? As chemists could see no reason for such regularity in the composition of matter the facts themselves were at first disputed, until repeated experiment rendered them incontrovertible. Assuming the constancy of proportion in chemical compounds, even before such constancy was proved, the English chemist John Dalton, sought an explanation in the following hypothesis, which has been accepted as a basis for chemical speculation ever since its establishment and which is here given in the form at present accepted.

Matter is not divisible *ad infinitum*, but is composed of very small and discrete entities called atoms, there being as many different kinds of these as there are varieties of substance which have never been decomposed into two or more forms with differing properties. The elements having weight, the atoms being portions thereof necessarily also have weight; and we assume the weight of an atom of a given element to be equal to that of each other atom of the same element, but to differ from that of an atom of any other element. The atoms of the elements unite to form the smallest individual group of the compound should they differ from each other, and of the element should these atoms be of the same kind; these groups are known as molecules, the agglomeration of which forms tangible matter. The weight of the molecule, known as the molecular weight, is therefore equal to the sum of the weights of its constituent atoms. If I mentally subdivide any given compound body, water for instance, I can continue the operation until I arrive at the smallest individual particle thereof, a molecule; if I divide this I no longer have water but two different kinds of matter, hydrogen and oxygen. This illustration will also serve to show the difference between a so-called chemical and a physical change. Water can be decomposed into its molecules with comparative ease, by changing it to steam, these are so far separated that they travel in right lines independently of each other. A much greater heat than was necessary for the production of steam or the application of some other form of energy, such as electricity, is necessary to effect any further change, and this brings with it the destruction of the nature of the substance. Water is no longer present, but in its place we have two different kinds of matter, hydrogen and oxygen, so that a chemical change has been produced.

With the atomic hypothesis in view the constant composition by weight of compound substances is readily explained. For instance a molecule of iron sulphide is composed of atoms of iron and sulphur, each molecule containing the same number of atoms. If all atoms of iron are alike in weight and if all atoms of sulphur bear the same relationship to each other, it follows that every molecule of iron sulphide must have the same composition as every other molecule of the same substance, and from this it follows that tangible quantities of the substance must have the same proportional composition by weight as the molecules. By accepting the theory as outlined the unvarying composition of purely chemical compounds of necessity follows. Of course two or more substances may be mixed in any proportion, but such a mixture does not have the characteristics of a chemical compound. The various constituents of such a mixture can be separated with greater or less ease by simple mechanical operations; as soon as a chemical compound is formed from the parts of any mixture a substance having a definitely constructed molecule results. We saw that iron and sulphur are however capable of forming two compounds with each other. In these two sulphides the relationship by weight which the quantities of sulphur bear to each other is as one to two, and it has been proved by repeated and painstaking experiment that a great number of similar cases exists in which an element forms two or more distinct compounds with some other element; in comparing such compounds the quantities in which the latter unites are in simple ratio to each other. The results of these discoveries can be summed up as follows in the law of multiple proportions.

"If two elements, *a* and *b* unite in more than one proportion, the parts by weight of *b* which will unite with a definite quantity of *a* will be in simple ratio to each other."

This law of multiple proportions is readily explained by the atomic hypothesis. For let us suppose, using the two sulphides of iron as an example, that the one composed of 28 parts of iron to 16 parts of sulphur has a molecule constructed of one atom of iron and one atom of sulphur. In order to change this molecule into one containing more sulphur the only possible means is by the addition of another atom of sulphur. But as the atoms of sulphur all have the same weight, it follows that the amount of sulphur in the newly formed molecule must be to that in the original as 2:1. We might represent the change graphically as follows, using the black circle to represent an atom of iron, the white one sulphur.

28 16 + 16 = 16 28 16

● ○ + ○ = ○ ● ○

Molecule of iron sulphide + 1 atom of sulphur = Molecule No. 2 of iron sulphide.

We could have come to the same conclusions, deducing the law of multiple proportions as a necessary consequence of the atomic structure of matter had we used combinations of any other elements; for the law is universal in its application. What is true of the individual molecule must also be true of tangible matter.

When the atomic theory as outlined had become a part of the belief of the greater number of chemists, the endeavors of investigators were in the direction of determining the weights which must be assigned to the various atoms, and as these determinations involved the most painstaking and difficult manipulation at that time required, it of necessity followed that wide differences of opinion, only disappearing within the most recent times were manifested; indeed absolute certainty is not even now attained or attainable as regards these constants. The absolute weights of the atoms, being extremely small fractions of a milligramme, were quantities not obtainable with any degree of accuracy, nor was it necessary to endeavor to make such determinations the relative weights answering all purposes of theory or investigation; so that the fixing of the latter became of paramount importance. The selection of a standard by which all other weights can be compared is as necessary in dealing with atoms as it is in the mensuration of distance, it being immaterial what standard is selected provided all of the weights can easily and accurately be compared with this. During the first years of our atomic hypothesis the weight of the atom of hydrogen, being the smallest appertaining to any element, was selected as unity, but subsequently this practice was abandoned in favor of oxygen, the weight of the atom of which was placed at one hundred. Hydrogen once more resumed its original position during the middle of the century and until recently all weights of atoms, technically known as atomic weights, were compared with this. If we call to our aid certain theories concerning the nature of gases, a consideration which must be deferred until the pupil has become acquainted with a larger number of chemical facts, we can place the ratio between the atomic weights of hydrogen and oxygen at from 1:15.87 to 1:15.96, numbers which very nearly coincide with 1:16. Considerable uncertainty exists as to the accuracy of this ratio, for recent investigation has altered these quantities repeatedly. If all atomic weights are referred to hydrogen as unity, a recalculation of these constants is necessary whenever investigation shows the accepted ratio to be untenable; for these quantities have been determined for the greater number of elements directly or indirectly by an investigation of compounds with oxygen. It seems more advisable, therefore, to adopt oxygen as a standard and, so as not to depart too far from numbers rendered familiar by accepted usage, to place this at 16. By this means the atomic weight of hydrogen becomes 1.007. If any further correction in the ratio between hydrogen and oxygen becomes necessary, such a change will involve no further calculation. The methods by which the atomic weights have been determined are not a subject for discussion at the present time, indeed, the great majority of them would be entirely out of place in an elementary treatise; suffice it to say that so complete has been their application that the weights which are placed in the following table are, with unimportant exceptions, accepted as correct by all chemists:

NAME.	SYMBOL.	ATOMIC WEIGHT.	NAME.	SYMBOL.	ATOMIC WEIGHT.
ALUMINIUM	Al	27.	Didymium	Di	142.3
ANTIMONY	Sb	120.	Erbium	Er	166.3
ARSENIC	As	75.	Fluorine	F	19.
BARIUM	Ba	137.	Gallium	Ga	69.
Beryllium	Be	9.	Germanium	Ge	72.3
BISMUTH	Bi	208.9	GOLD	Au	197.3
BORON	B	11.	HYDROGEN	H	1.007
BROMINE	Br	79.95	Indium	In	113.7
Cadmium	Cd	112.	IODINE	I	126.85
Caesium	Cs	132.9	Iridium	Ir	193.1
CALCIUM	Ca	40.	IRON	Fe	56.
CARBON	C	12.	Lanthanum	La	138.2
CERIUM	Ce	140.2	LEAD	Pb	206.95
CHLORINE	Cl	35.45	LITHIUM	Li	7.02
CHROMIUM	Cr	52.1	MAGNESIUM	Mg	24.3
Cobalt	Co	59.	MANGANESE	Mn	55.
Columbium	Cb	94.	MERCURY	Hg	200.
COPPER	Cu	63.4	Molybdenum	Mo	96.

NAME.	SYMBOL.	ATOMIC WEIGHT.	NAME.	SYMBOL.	ATOMIC WEIGHT.
Nickel	Ni	58.7	Strontium	Sr	87.6
NITROGEN	N	14.03	SULPHUR	S	32.06
Osmium	Os	191.7	Tantalum	Ta	182.6
OXYGEN	O	16.	Tellurium	Te	125.
Palladium	Pd	106.6	Terbium	Tb	159.5
PHOSPHORUS	P	31.	Thallium	Tl	204.18
Platinum	Pt	195.	Thorium	Th	232.6
POTASSIUM	K	39.11	Tin	Sn	119.
Rhodium	Rh	103.5	Titanium	Ti	48.
Rubidium	Rb	85.5	Tungsten	W	184.
Ruthenium	Ru	101.6	Uranium	U	239.6
Samarium	Sm	150.	Vanadium	V	51.4
Scandium	Sc	44.	Ytterbium	Yb	173.
Selenium	Se	79.	Yttrium	Yt	89.1
SILICON	Si	28.4	ZINC	Zn	65.3
SILVER	Ag	107.92	Zirconium	Zr	90.6
SODIUM	Na	23.05			*

The ratio of hydrogen to oxygen is 1:15.88. The term glucinum is frequently used instead of beryllium. The more important elements are in large type.

We are acquainted with sixty-seven different kinds of matter, none of which have ever been decomposed into two or more simpler forms; but, whether such decomposition will ever occur, it is impossible to state. By the union of these elements all substances known to us are produced. By far the greater proportion of matter, being composed of molecules containing two or more atoms differing from each other in kind, is compound in its nature. The individual atoms do not, except in rare instances, exist as such; they are united to form molecules, the difference between the molecule of the element and that of the compound being that while in the former the atoms are all of the same kind, in the latter they differ. Atoms are grouped together to form molecules which are more or less stable, and this stability must be effected by some force, which has been compared to the attraction of gravitation and has, by some, been considered identical with it, acting between the individual atoms. The attraction of gravitation, however, is capable of manifestation between bodies at a great distance from each other, while the number of bodies acted on, in this manner, by any given body is unlim-

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*As a matter of expediency the pupil should memorize the atomic weights of a few of the more important elements. The acquirement of this knowledge is best deferred until the individual elements are discussed, when the weights can be learned during the progress of the study.

ited. The attraction between the atoms seems capable of manifestation only through an extremely small interval of space, and then only between a limited number of atoms. A new term is therefore necessary to designate this force which holds the atoms in position in the molecule, and for want of better ones the expressions "chemical affinity" or "chemism" are used. Where a very stable compound exists, the atoms composing it are said to have a great affinity for each other; and an inquiry into the relative stability of chemical compounds is one of the greatest importance and consequently will frequently be made during the progress of the work; but it must not be forgotten that the term "chemical affinity" is used simply to designate a force which has never been resolved into simpler factors, and of the nature of which we are consequently ignorant.

A substance which is capable of performing work possesses energy, and the atoms possess energy because they are, in uniting, capable of performing work by reason of their chemical affinity. Illustrations of this performance of work by the union of atoms are to be seen by us at all times; thus the motions of machinery driven by steam can with the greatest ease be traced to the chemical union of the oxygen of the atmosphere with the coal under the boilers and the movements of animals can in the same way be shown to be derived from the chemical energy of the various substances which form the nutriment of the body. The energy possessed by the individual atoms can be likened to potential energy (energy of position) for by its means the atoms are capable of performing work just as is a stone when raised above the level of the earth.

The measure of work is the force (P) which overcomes resistance, into the distance (S) through which this force acts ($L = P S$). The amount of work which a body is capable of performing by reason of its position is called its potential energy. If the work (L) of the force (P) is neutralized by a negative force (P'), L is not lost for P can perform its work (L) as soon as P' ceases to act. A body of the weight P which has been lifted through the distance S has an amount of potential energy equal to $P S$, for as soon as it is dropped it can perform the work $P S$. The energy possessed by the atoms is to us different from potential energy because it has never been resolved into the factors $P S$. The amount of work which a body in motion is capable of performing by reason of that motion is called its kinetic energy (energy of motion). This is equal to one-half the product of the mass of the body and the square of its velocity ($L = \frac{m v^2}{2}$). If a part of the potential energy possessed by a body has been used and thereby a certain amount of kinetic energy has been produced, then the sum of the remaining potential energy and of the produced kinetic energy is equal to the original amount of potential energy; or, what is the same thing, equal to the kinetic energy which would have been produced if the entire store of potential energy had been used to perform work. If the stone, which we had supposed to be suspended, had been allowed to fall to the ground, the entire contents of potential energy would have been changed to heat, which is a form of kinetic energy. These few remarks illustrate the principle of conservation of energy which was defined by Mayer in 1842. What is true of the stone is also true of the atoms, for their potential energy, or better chemical energy, a term which will involve us in no contradictions, can be transformed into kinetic energy upon their union to form a compound. While we cannot measure the amount of chemical energy possessed by the atoms, we are able to measure the kinetic energy which is produced when they unite by reason of their chemical affinity, for by far the greatest amount is manifested as heat. If the stone, which we have used as an illustration, falls through a certain distance its potential energy is converted into kinetic energy and to once more raise this stone to its original position will require an equivalent expenditure of work. Just so with the atoms. If two atoms have a great chemical affinity for each other they possess a great amount of chemical energy which will be converted into an equally great amount of kinetic energy when they unite, and in order to separate the molecule so formed into the original atoms we will have to apply the same amount of energy in some form; the molecule is as a consequence stable and possesses an amount of chemical energy much smaller than that of its constituent atoms. On the other hand two or more atoms may possess very little chemical affinity for each other, so little indeed, that an expenditure of energy is necessary to cause them to unite, therefore the molecule caused by such a union will have a tendency to readily convert its acquired chemical energy into some form of kinetic energy, and will be unstable. Molecules which have been formed with an evolution of heat, and which therefore possess less energy than their constituent atoms, are said to be the product of an exothermic reaction; while those which have resulted from an absorption of heat are the result of an endothermic one. The heat given off or absorbed in these changes has in many cases been measured and is taken as an indication of the chemical affinity of the atoms. The elements show great variations in this respect, some have a great chemical affinity for each other and thus form stable compounds, others have very little, while some have none at all, in which case no expenditure of energy will cause them to unite. We must bear in mind that any given element varies much in its affinity toward the various other elements, and also that what we have explained as regards compounds formed between individual atoms is true as regards compounds formed from two or more molecules. The various phases of chemical reaction which we shall study will give us abundant opportunity of returning to this subject.

The elements are divided into two classes, the most marked representatives of each of which exhibit the sharpest possible chemical contrast toward the other; one of these classes is familiar to all of us, it is that of the metals, with the superficial qualities of which, such as metallic lustre, malleability and ductility, we are tolerably well acquainted, while in addition to these properties metals are also as a rule good conductors of heat and of electricity. At the opposite chemical extreme we find a class of elements which can best be described as not-metals. A few of these are gases and thereby they differ from the metals, only one of which, hydrogen, exists in this state at ordinary temperatures. The not-metals, where solid, are colored bodies which are brittle, neither malleable or ductile, and either non-conductors of electricity and poor conductors of heat, or at least they possess these two properties in a degree much inferior to the metals. A number of not-metals on superficial examination will appear to have metallic lustre, yet a closer inspection reveals the fact that this is only apparently the case, for in forming a section of the element we find the same to be capable of transmitting light even through some considerable thickness. Between the two extremes we have a considerable number of elements which may have the characteristics of both metal and not-metal, such as arsenic and tellurium which, while possessing a distinctly metallic appearance, have chemical characteristics which would cause them to be more properly classed as not-metallic substances. The most pronounced metallic elements have a marked chemical affinity for the characteristic not-metals and form stable compounds therewith, the less apparent the contrast in the elements the more easily decomposed will in many cases the compound resulting from the union of such elements be, yet such a statement as this must not by any means be taken as a general rule; for we find the most stable compounds resulting from the union of atoms of the same element, as in the molecules of chlorine and hydrogen, and also from elements which closely resemble each other, as in the compounds of sulphur and oxygen. If a compound formed of a metal and a not-metal is subjected to the action of an electric current the metal will separate at the negative pole, the not-metal at the positive one, and for this reason the metals are called electro-positive, while the not-metals are electro-negative. This rule was formerly supposed to be universal in its application and a system of chemistry was then established by which it was believed that all compounds were first formed by the union of a negative and a positive element to form a molecule, and then by the union of a negative and positive molecule to form a more complex substance. While the negative or positive character of the elements composing a compound is undoubtedly of great influence upon their nature, a system founded exclusively on these characteristics has proved untenable; convenience however, causes us to retain the expressions "negative" and "positive," the term negative being used to designate all of the properties which characterize the not-metal, and the term positive those of the metal.

There are certain. chemical characteristics which enable us to draw the line between metal and not-metal with tolerable distinctness. The metals all form compounds with oxgen, the not-metals with two exceptions, fluorine and bromine, do the same, these compounds are known as oxides. The oxides of the metals in most cases are classed as bases, a term which is also applied to compounds of the metals with oxygen and hydrogen, the oxides of the not-metals are termed the anhydrides of acids, where on addition of water they are capable of forming acids. The contrast between metal and not-metal becomes apparent when these oxides interact chemically, for a new compound, a salt, is produced. Thus the oxide of potassium, a base, when brought in contact with the oxide of sulphur, an anhydride known as sulphur trioxide, produces a salt, the sulphate of potassium. We will have occasion to more thoroughly comprehend the meaning of these terms as we become more acquainted whith chemical facts.

The writing of the innumerable chemical changes which take place would be complicated, and a coördination of the phenomena rendered difficult were not some system of notation employed by chemists which would express the reactions without the trouble of writing in full the names and atomic weights of the various elements. Feeling this need, some designation of the elements by signs has since the time of the alchemists been employed. The system introduced by the Swedish chemist Berzelius, in use at the present time, is the one which has been found to best answer all requirements. By means of this the various elements are designated by the first letter of their english or latinized name in capitals or, where conflict would arise, by the first letter of the name in capitals followed by some other letter usually the next following, in small type. Thus hydrogen has the symbol H, oxygen, O, sodium, Na, from the latinized natrium, mercury, Hg, from the latin hydrargyrum. These symbols do not stand for the visible elements but represent the atoms of the elements, and hence include the idea of atomic weights. Thus O, stands for an atom of oxygen, and means that as the atom of oxygen is sixteen times as heavy as the atom of hydrogen, we have sixteen times as much oxygen by weight as hydrogen when the latter is expressed by the symbol H. By writing the symbols side by side we express a chemical compound, as for instance H_2O, which stands for the chemical compound water, the number two placed after and below the letter H, meaning that in water there are two atoms of hydrogen, the whole combination meaning that in H_2O, we have two atoms of hydrogen united to one of oxygen in the ratio of 2 to 16 by weight, H_2O being called the formula of water and the sum of the atomic weights, represented by 18, the formula weight. In the case of water, and in the case of many other substances which can be obtained as gases, this formula weight is also the weight of the molecule, and is hence the molecular weight. The combination *NaCl* means that one atom of sodium is united to one atom of chlorine to form the compound sodium chloride, at the same time it indicates that twenty-three parts by weight of sodium are united to thirty-five and a half parts of chlorine, these numbers representing the atomic weights of sodium and chlorine respectively. Whether *NaCl* represents the molecular weight of sodium chloride we cannot state, for the substance may be composed of molecules formed by the union of a number of formula weights *NaCl*, however it is extremely probable that, if such be the case, the molecule of sodium chloride is produced by the union of a number of entities which all have the composition *NaCl*, and there is no great objection against using the terms molecular weight and formula weight interchangeably in the majority of cases.

Our present knowledge seems to show that the total amount of matter contained in the universe never varies. The atoms composing chemical compounds may change their position or manner of grouping, they may be transferred from one compound to another, or the compound may be decomposed into its elements but the atoms can neither be created or destroyed. The entire science of chemistry is based upon this law of the indestructibility of matter which was first understood by Lavoisier, and every chemical change since his time has but served to prove its existence. As a consequence the compounds produced by the interaction of elements must equal in weight the amounts taken before the reaction, and the sum of the weights of the elements or compounds produced by the decomposition of a compound substance must equal the weight of the substance originally employed. Our symbols being used to express weights as well as other characteristics of the elements it follows that we can bring any chemical reaction into the form of an equation; thus $H+Cl=HCl$ means that hydrogen plus chlorine yields a compound of hydrogen and chlorine, hydrochloric acid, and the atomic weight of hydrogen being in round numbers one, it also means that 1 part by weight of hydrogen plus 35.5 parts by weight of chlorine, (the latter number being the atomic weight of that element,) equal 36.5 parts by weight of hydrochloric acid.

The formula $HgO=Hg+O$ indicates that the oxide of mecury is decomposed into mercury and oxygen and that the weight of the oxide of mercury is equal to the sum of the weights of oxygen and mercury produced.

$$C_2\,O_4\,H_2=CO_2+CO+H_2O$$

means that a compound of carbon, hydrogen and oxygen (oxalic acid) can be decomposed into CO_2 (carbon dioxide), CO (carbon monoxide) and H_2O (water), and that the weight of the oxalic acid taken is equal to the sum of the weights of CO_2, CO and H_2O produced. The atomic weights of carbon, oxygen and hydrogen are 12, 16 and 1 respectively, hence $(2\times 12)+(4\times 16)+2=90$ parts by weight of oxalic acid yield, $44+28+18=90$ parts by weight of CO_2, CO and H_2O.

Some doubt will arise in the beginner's mind as to the legitimacy of the numbers used as atomic weights; he will naturally ask, why is the atomic weight of carbon 12 and not 6? Why for instance, should we suppose the formula of carbon dioxide to be CO_2 and not C_2O_2? These very doubts were entertained by chemists during the first six decades of the century, and only by painstaking investigation with the aid of a number of physical laws have they been removed. At the present period of our study we must accept the atomic weights as they are given, a discussion of the various reasons for this acceptance would be far beyond the scope of an elementary treatise; but such as can properly be produced will be introduced at a subsequent time. Chemists, as a rule, are skeptical to a degree, and the fact that our present atomic weights are believed in by the great majority must be a sufficient guarantee for their accuracy. The pupil must remember that chemical symbols stand for material substances, he must not be led to consider the element nitrogen for instance, as being simply the symbol *N*, nor potassium, the symbol *K*, but should always bear in mind that these letters stand for existing elements endowed with various properties, which would remain even if no system of chemical notation had ever been established.

The elements are by no means substances any one of which differs from all others; indeed, no one element exists which does not exhibit characteristics which mark its resemblance to a number of its fellows. Roughly speaking the elements are divided into metals and not-metals, the metals all bearing a certain resemblance to each other, and the not-metals all being more or less alike, yet both metals and not-metals are naturally divided into groups the individual members of which all have a strong family likeness, while these various groups also have a number of points in common; and we shall see that by arranging the elements in the order of their atomic weights, beginning with that having the smallest number, this resemblance will become most apparent. By constructing a table of the elements arranged in this manner we have produced a system of classification a careful study of which has shown us that the characteristics of any element are determined by the atomic weight of that element; so that if we are thoroughly familiar with this arrangement we can without any previous knowledge of its chemical deportment describe with tolerable accuracy the properties of an element, with the atomic weight of which we are acquainted. This system will provide the order in which the various elements will be discussed.

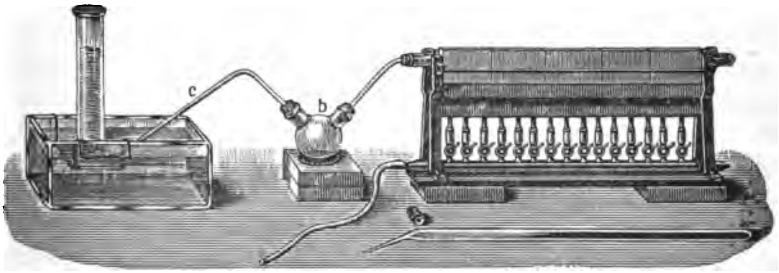
Having by this brief introduction learned some of the fundamental theories upon which our science is based, we will now go on to the special descriptive portion of chemistry. In so doing we will find it expedient to first become acquainted with a typical not-metal, then with a metal, and immediately following with the compound produced by the chemical union of these two contrasting elements. The not-metal will be oxygen, the metal, hydrogen, and the compound, water.

CHAPTER II.

OXYGEN.

Symbol O, atomic weight, 16, Specific gravity, air = 1, is 1.10563, H = 1, is 15.88; 1 c. c. O at 0° and .76m pressure .0014303 gram.

Oxygen is the element which occurs in greatest quantity upon our planet; it forms about 47.3 per cent. of the solid portion of the earth, 85.8 per cent. of the ocean and, including its occurence in the atmosphere, about 50 per cent. of the total substance of the globe. In the atmosphere it is found as uncombined oxygen, mixed with nitrogen and a few other gases, furnishing one-fifth of the entire gaseous envelope of the earth. It is found united with hydrogen in water, forming eight-ninths of that substance; by far the greater portion of the crystalline rocks contain oxygen, combined with other elements; the soil and the various forms of vegetable and animal life contain this element chemically combined, and also to some extent as free oxygen.



Oxygen was isolated on August 1st, 1774, by an English chemist, Joseph Priestley, who prepared it by heating "red precipitate" (red oxide of mercury), placing this substance in the focus of a burning glass exposed to the sun's rays. He termed the gas deplogisticated air, because, according to the theory then held, a substance, in burning, gave off an hypothetical principle, called phlogiston, subsequently thought to be identical with hydrogen. As oxygen was capable of supporting combustion in a very energetic manner, it was supposed that the element must necessarily be able to take the phlogiston from the burning substance, and from this property the gas received its first name.

The methods of its preparation are as follows:—

Red oxide of mercury is heated in a hard glass tube[1], when it breaks down into mercury and oxygen. The formula of this oxide is HgO, which means that in one formula weight of mercuric oxide there are united one atom of mercury and one of oxygen. The reaction is represented as follows:—$HgO = Hg + O$. The atomic weight of mercury is 200, that of oxygen 16: hence the equation indicates that 216 parts by weight of the oxide of mercury yield 200 parts of mercury and 16 parts of oxygen upon heating.

Black oxide of manganese (manganese dioxide,)[2] is heated in an iron tube, the oxygen so prepared being collected over water.[3]

The reaction is as follows:

$3\,MnO_2 = Mn_3\,O_4 + 2\ O$; the substance formed is an oxide of manganese containing less oxygen than MnO_2. As one formula weight of Mn_3O_4 contains three atoms of manganese, it follows that, in writing the equation, three times one formula weight of MnO_2 must be used, and this is indicated by placing the coefficient 3 before the formula MnO_2. As the atomic weight of manganese is 55, it follows that 261 parts by weight of manganese dioxide yield 229 parts of Mn_3O_4 and 32 parts of oxygen. From the examples cited, the meaning of chemical equations will be sufficiently understood so that the student, by consultation of the table of atomic weights, will be able to determine the relations by weight in all others. We will therefore, in the future, be contented with writing equations without indicating the quantities of the substances reacting.

Neither of the methods which have been given are of great practical use in the preparation of oxygen. Better results are obtained by heating chlorate of potassium, a white crystalline substance somewhat resembling common salt,[4] in a flask connected with a delivery tube, as in Fig. 2. Chlorate of potassium breaks down as follows: $KClO_3 = KCl + 3O$.* (Chlorate of potassium yields potassium chloride and oxygen.) The most approved method of preparing oxygen for laboratory use is by heating a mixture of chlorate of potassium and manganese dioxide, the apparatus used being the same as for that of the previous experiment.[5] By this means the oxygen passes off at a much lower temperature, and quite regularly. The part which the manganese dioxide plays in the reaction is not as yet definitely understood, for it remains as manganese dioxide in the final result. It is not improbable that the substance takes up oxygen from the chlorate of potassium, thus forming an oxide of manganese containing more oxygen than does MnO_2 (a so-called higher oxide,) which then readily breaks down into manganese dioxide and oxygen, the black oxide of manganese thus acting as a conveyer of oxygen. Substances which act in this manner, their influence not being clearly understood, are said to act by catalysis. All of the reactions cited have one thing in common; the substances decomposed contained oxygen which was driven off by heat, there remaining either elements or compounds containing less oxygen than the original material. As energy was added to effect the separation, the substances produced contain a greater

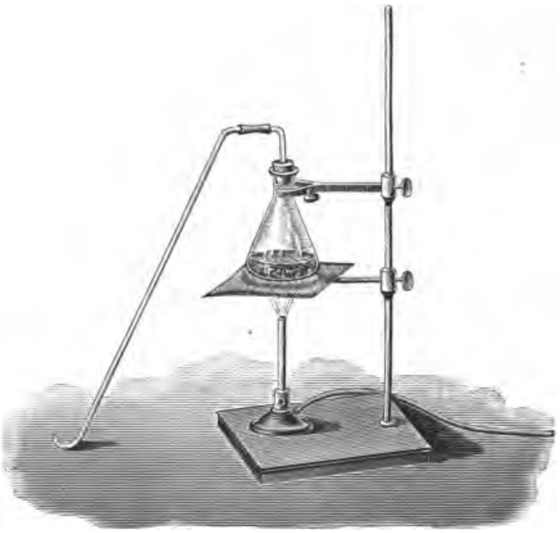


FIGURE 2.

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* The reaction as represented gives the final result obtained by heating chlorate of potassium. There is an intermediary product formed for which see chloric acid. The pupil should by means of the table of atomic weights determine the relationships by weight in this and in a large number of subsequent equations.

amount of chemical energy than those employed, while all of these reactions belong to those classed as chemical analyses.

Oxygen is a colorless, odorless and tasteless gas, which is converted to a liquid by a pressure of 50 atmospheres at a temperature of —118°. A certain temperature exists, constant for any given gas but varying with different gases, above which they cannot be liquified by any pressure. This temperature is called the critical temperature, for oxygen it is at —118°. Liquid oxygen boils at —181° at 740 mm. pressure. Oxygen is but slightly soluble in water, 100 volumes of that liquid dissolving 4.1 volumes of oxygen at 5°.* Small as this amount is, it is sufficient to furnish the material required by fishes for their physiological functions, and this solubility is therefore of the highest importance; water containing no oxygen is unable to support marine life.

Oxygen forms chemical compounds, called oxides, with all other elements excepting fluorine and bromine, and it will combine with the latter element provided some positive element is also a constituent of the compound. In the formation of many of the oxides a great amount of heat is produced so that the substance, whether a burning solid or a vapor, will begin to glow much more intensely in oxygen than in the air. That this is the case may be proved by placing a glowing pine chip in a jar of oxygen, when the wood will at once burst into flame. When the changes which take place in the burning in oxygen of the few substances which we have space to consider are studied, it should be remembered that phenomena similar to those which will be described take place in a large number of cases. A piece of phosphorus ignited and placed in the gas will continue to burn with a dazzling white light,[6] forming white fumes of the oxide of phosphorus. The reaction which takes place is as follows:

$2\ P+5\ O=P_2\ O_5$, a white solid substance, phosphorus pentoxide, is produced; this is readily soluble in water, and when so dissolved forms phosphoric acid. Sulphur, which has been ignited will burn in oxygen with great energy and with a brilliant blue flame, the product of the combustion being a gas, sulphur dioxide, ($S\,O_2$):

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*By this expression is meant that 100 liters of water would disolve 4.1 liters of the gas.

$$S+2\,O=S\,O_2.$$

A piece of glowing carbon becomes brightly incandescent when placed in oxygen, the substance burning to form a gaseous compound, carbon dioxide, ($C\,O_2$):—

$$C+2\,O=C\,O_2.$$

The three oxides produced by the above reactions are oxides of not-metals and hence bear the characteristics of the anhydrides of acids. (See page 13).

Even substances, such as iron, which we do not ordinarily consider as combustible, burn readily in oxygen. If a steel watch spring is heated[7] and placed in a jar of the gas, the substance will continue to burn, sparks of the oxide of iron being thrown about the jar.

$$3\,Fe+4\,O=Fe_3O_4*$$

From these few examples we can form some idea of the readiness with which oxides are formed, and what is true of the elements referred to, also hold good with a large number of other ones when they are heated in oxygen gas. In a restricted sense, the term combustion refers only to the union of various substances with oxygen, with the evolution of light and heat. During any chemical process, in which two elements directly unite, heat is liberated, but if the union of a body with oxygen takes place slowly, so that in any given interval of time only very small amounts of the substances under consideration were to unite, we might not be able to note any increase of temperature, for the inconsiderable quantity of heat given off in this period is conducted away by the surroundings. The rusting of iron consists of such an oxidation, without any perceptible rise in temperature, it is, nevertheless, just as much a form of combustion as the more rapid and brilliant one referred to above. It follows that combustion may be either slow or rapid. A substauce must be heated to a certain temperature before slow can be converted into rapid combustion, and this is called the kindling temperature. The kindling temperature varies for different substances, but is the same for any given substance, and if, moreover, the burning body be cooled below that point, an extinction of the fire results. We have daily evidence of this in the blowing out of lamp flames, which simply consists in cooling the gases which form the flame below the kindling temperature; while, on the other hand, the application of a lighted match to a gas burner only serves to heat the escaping gases to their kindling temperature. If a substance is undergoing slow combustion, in such a situation that the heat given off cannot be readily conducted away, the temperature of the whole will gradually rise until the kindling point is reached, and in this manner spontaneous combustion takes place in heaps of oiled rags, where the oil is being slowly oxidized by the oxygen in the atmosphere. Substances, which are capable of oxidation, possess a certain amount of chemical energy in the presence of oxygen and, in uniting, this energy is converted into heat; but, as the amount of energy in any given body must be constant before combustion, no matter whether the process is to be slow or rapid, therefore, provided the products of combustion do not vary, it follows that the amount of heat liberated must be the same in either case. It sometimes occurs, however, that the substances formed by slow combustion may be chemically different from those by rapid, when, of course, the amount of heat liberated would depend upon the product formed.

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* The oxide $Fe_3\,O_4$, occurring as the mineral magnetite, is the oxide of iron always formed at high temperatures, when the metal is heated in the presence of oxygen.

It would be erroneous to suppose that the phenomena of combustion are only apparent when oxygen is taking part in the performance, for, as the process of direct chemical union between two bodies is always accompanied by heat, it follows that, in the union of other elements or compounds, this may be so great that the substances reacting begin to glow or burst into flame. Thus, for instance, hydrogen can burn in chlorine just as readily as the same substance burns in oxygen, so that, in the very broadest sense, combustion would refer to the union of any substances with the evolution of heat. This very broadening of the sense, however, would rob it of its significance, so that the term combustion might perhaps preferably refer only to the union of any substance with oxygen and with the evolution of light and heat, while, instead of slow combustion, the term slow oxidation, or, in the case of other elements, some more particular term would have a more distinctive meaning.

Two elements which are cabable of directly uniting must possess a certain amount of chemical energy, just as a stone raised above the ground possesses potential energy, and the chemical energy is converted into heat on union, just as the potential energy of the stone was changed to kinetic on falling. Now, after the stone has fallen, it requires just as much energy to once more bring it back to its original position as was given off by it in its descent. Just so with chemical compounds. In order to decompose them, as much energy must be added as was given off in their union. Therefore, in decomposing a body formed by combustion or slow oxidation, just as much heat, or other form of energy, must be applied as was given off. The heat of decomposition being thus equal to the heat of formation; it follows that those bodies which burn energetically in oxygen, with the evolution of much heat and light, will necessarily form stable oxides by their union.

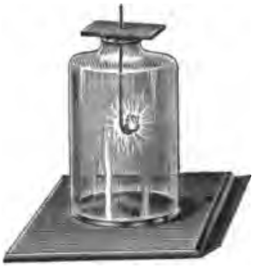

FIGURE 3.

The bodies formed by the union of oxygen with other elements are termed oxides, and we are acquainted with the oxides of all elements excepting those of fluorine and bromine. The greatest diversity of characteristics exists among these chemical substances, but as we have seen in the introduction, they can in most instances be classed either as bases or as anhydrides of acids; the bases being oxides of metals which will exhibit the same contrast toward the oxides of not metals, called anhydrides, as the metal itself does toward the not-metal, with the sole exception that this contrast is intensified by the addition of oxygen to the not-metal in the formation of the anhydride. The result of the chemical union of base and anhydride is a salt, usually possessing somewhat indifferent chemical properties, and the product of the union of metal with not-metal not infrequently has the characteristics of a salt, as for instance common salt, or sodium chloride, $Na\,Cl$. Examples of the oxides of metals which are bases, are $Zn\,O$, zinc oxide, $Na_2\,O$, sodium oxide, $Mg\,O$, magnesium oxide; examples of the anhydrides of acids are $S\,O_3$, sulphur trioxide, $P_2\,O_5$, phosphorus pentoxide, and $C\,O_2$, carbon dioxide, and the production of salts from the union of these two contrasting substances can be represented as follows:

$$\overset{+}{Zn}\,O+\overset{-}{S}\,O_3=Zn\,S\,O_4\text{, Zinc Sulphate.}$$

$$3\,Na_2\,\overset{+}{O}+\overset{-}{P_2}\,O_5=2\,Na_3\,P\,O_4\text{, Sodium phosphate.}$$

$$\overset{+}{Mg}\,O+\overset{-}{C}\,O_2=Mg\,C\,O_3\text{, Magnesium Carbonate;}$$

and if we compare these reactions with the formation of common salt from sodium and chlorine:—

$$\overset{+}{Na}+\overset{-}{Cl}=Na\,Cl\text{, Sodium chloride,}$$

the similarity in the formation of salts from the two contrasting compounds, and from two contrasting elements is quite evident.

There are in addition to the oxides referred to above, a large number which are neither basic nor acidic. To this class belong the oxides known as hyperoxides, of which manganese dioxide is an example. All of these have the metallic character of the metal about neutralized by the not-metallic oxygen, so that where they are capable of taking up more oxygen, upon such addition the resulting compound bears the characteristics of the negative anhydride of an acid, and when they lose oxygen to form a lower oxide the resulting substance has more or less the characteristics of the base. They are on the turning point from base to anhydride, and all of them lose a part of their oxygen readily, as did manganese dioxide. A number of the oxides of the not-metals also are not anhydrides of acids and hence do not unite with the bases to form salts. All of these oxides contain but little oxygen, as for example CO, carbon monoxide, $N_2\,O$ nitrous oxide.

Many of the elements are capable of forming a number of oxides, nitrogen can even form five of these, varying in character with the increase of oxygen. A number of metals can form two oxides, both of which are bases, and in such a case the oxide containing the lesser amount of oxygen relatively to the quantity of metal is designated by the suffix *ous* attached to the name of the metal, the one containing the greater by *ic*, thus copper forms two oxides, $Cu_2\,O$, cuprous oxide, $Cu\,O$, cupric oxide; iron has the same property so that the two oxides $Fe\,O$ and $Fe_2\,O_3$ are termed ferrous and ferric oxides respectively; mercury can form $Hg_2 O$ and $Hg O$, mercurous and mercuric oxides; and the salts derived by the union of these oxides with the anhydrides of acids are designated in a similar manner; as $Fe SO_4$, ferrous sulphate, $Fe_2 (SO_4)_3$, ferric sulphate, so that the suffix *ous* indicates, where attached to the name of the metallic element in a salt, that this salt is derived from an oxide with less oxygen than some other oxide of the same element which can also act as a base.

CHAPTER III.

HYDROGEN.

Symbol H, atomic weight 1.007, Specific gravity, air = 1, is .06909 1 c.c. H weighs .0000895 grams at 0° and .76 meters pressure.

Free hydrogen is found only in small quantities in nature, notably in the gases which escape from petroleum wells, in natural gas, and in the gaseous exhalations of some volcanoes. It is said to have been found in a condensed state in some meteorites and it is frequently given off in processes of fermentation and decay. The element is, however, contained in enormous quantities in the chromosphere of the sun, the protuberances observed during eclipses consisting, for the greater part, of hydrogen; the temperature of the sun being so high that chemical union is impossible, its atmosphere consists of hydrogen, which is subjected to intense local disturbances. The fixed stars, Sirius for example, also contain large quantities of uncombined hydrogen, but the total amount of free and combined hydrogen on the earth is only about 1 per cent. of the entire mass.

Hydrogen was first described as a peculiar form of air by Cavendish in 1766, although it had previously been observed by Paracelsus, who obtained it by the action of dilute acids on certain metals, but confused it with other combustible gases. By Cavendish, Priestley and contemporaneous chemists, it was at one time considered as pure phlogiston, the element which was supposed to be given off by substances in burning. Lavoisier explained the composition of water at a later date, showing it to be an oxide of hydrogen, and thus proved that the element was a substance which could act like other elements, and was not phlogiston. Lavoisier gave this substance the name of hydrogène (from ὕδωρ water and the root γεν to produce) as water is produced by burning the gas in air or oxygen.

The methods of preparation of the element are as follows:

By the decomposition of water by means of the electric current, when hydrogen separates at the negative pole and oxygen at the positive one. The apparatus used in performing this experiment will be seen in Fig. 4.* †. $H_2O = 2H + O$.

The most pronouncedly metallic elements, such as sodium and potassium, have such a great affinity for oxygen that they can expel hydrogen from water at ordinary temperatures; for if a piece of sodium the size of a large pea is placed in water, a violent reaction[8] takes place, the heat evolved melting the sodium floating on the surface, while hydrogen is given off. If the water is thickened by starch paste, so that the molten metal cannot move freely on the

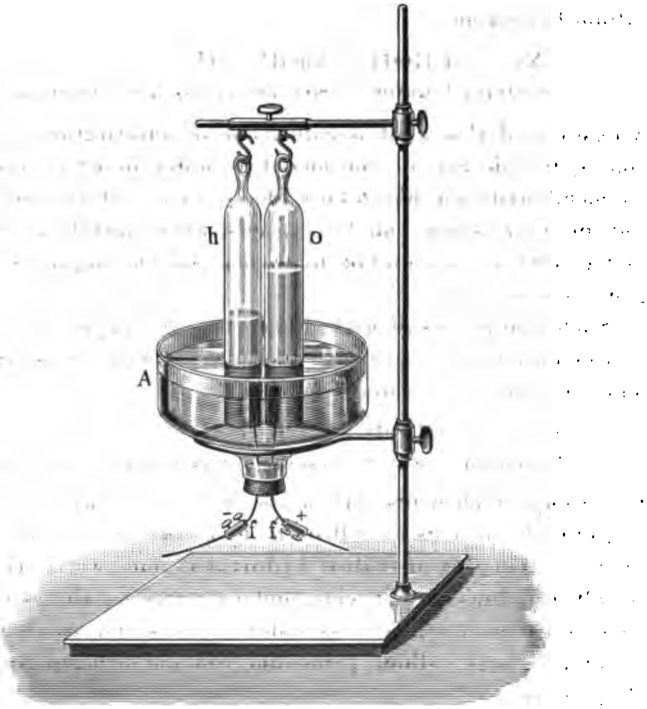

FIGURE 4.

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[*] Pure Water is a non-conductor of electricity, or at least very nearly a non-conductor, and hence a little sulphuric acid must be added to the water before performing the experiment.

[†] It will be noticed that for each cubic centimeter of oxygen liberated at the positive pole we have 2 c. c. of hydrogen formed at the negative.

surface, the hydrogen will be heated to its kindling temperature and take fire. Hydrogen can be collected by this method by placing the sodium in a wire spoon under the surface of the water in a pneumatic trough and inverting a test tube filled with water over the same, bubbles of hydrogen arise and soon fill the tube. The method is depicted by Fig. 6.[9] The water in which the sodium has been dissolved has a soapy feeling and an alkaline taste; it contains sodium hydroxide.

$$\text{Na} + \text{HOH} = \text{NaOH} + \text{H}.$$
$$\text{Sodium} + \text{water} = \text{Sodium hydroxide} + \text{hydrogen}.$$

A reaction of this kind is called one of substitution, for the sodium hydroxide can be considered as water in which one atom of the metal hydrogen has been replaced by one of the metal sodium, and similar reactions can be expected where metals are brought in contact with a compound of hydrogen and any negative element or group of elements.

Such changes result with other elements, the metallic properties of which are as pronounced as those of sodium; for instance, potassium will react with water as follows:[10]

$$\text{K} + \text{HOH} = \text{KOH} + \text{H}.$$
$$\text{Potassium} + \text{water} = \text{potassium hydroxide} + \text{hydrogen}.$$

The group of elements OH, where it is united with some element or group of elements, is called the hydroxyle group, and substances which contain this are called hydroxides, thus, water, HOH, could be called hydrogen hydroxide, and by replacing the hydrogen with some other element, such as sodium, potassium, calcium or magnesium, we have sodium, potassium, calcium or magnesium hydroxide produced.

NaOH, Sodium hydroxide,	Mg(OH)_2, Magnesium hydroxide.
KOH, Potassium hydroxide,	Fe(OH)_2, Ferrous hydroxide.
Ca(OH)_2, Calcium hydroxide.	Zn(OH)_2, Zinc hydroxide.

These hydroxides vary in formula, by reason of the fact that different metals are capable of uniting with different numbers of hydroxyle groups. In the examples before us we have two elements, sodium and potassium, which unite each with one hydroxyle group; two elements, calcium and magnesium, which unite with two, and we can cite a third class of elements, of which iron and aluminium are representatives, in which one atom of the metal can unite with three of these groups.

$Al(OH)_3$, Aluminium hydroxide,
$Fe(OH)_3$, Ferric hydroxide.

The hydroxides of the metals as well as the oxides are *bases* and with acids they yield salts and water, they therefore present the same chemical contrast toward anhydrides of acids or acids as did the oxides, thus:

$K_2O + SO_3 = K_2SO_4$
Potassium oxide + Sulphuric anhydride = Potassium sulphate.

$2KOH + SO_3 = K_2SO_4 + H_2O$
Potassium hydroxide + Sulphuric anhydride = Potassium sulphate and water.

$K_2O + H_2SO_4 = K_2SO_4 + H_2O$
Potassium oxide + Sulphuric acid = Potassium sulphate + water.

$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O$
Potassium hydroxide + Sulphuric acid = Potassium sulphate + Water.

The acid employed in the last two reactions is however nothing but sulphuric anhydride plus water, $SO_3 + H_2O = H_2SO_4$, so that both the oxide and hydroxide of potassium with either the anhydride of sulphuric acid or the acid itself will yield a salt, potassium sulphate, and water; except in the case of the oxide of potassium and sulphuric anhydride when the salt alone is formed. What is true of potassium is true of other metals as well. The oxides and hydroxides of the metals are therefore bases where with acids they yield salts and water; but the hydroxyle group is not confined in its union to metals alone, the not-metals likewise are capable of forming hydroxides, but the hydroxides of not-metals are acids; the discussion of these hydroxides is however better deferred until the pupil becomes acquainted with a greater number of chemical compounds.

The more pronouncedly metallic in its nature a metal is, the more readily will it be able to decompose water, liberating hydrogen. Sodium, potassium or calcium, do so at ordinary temperatures; magnesium does so, provided the water is boiling; iron, provided the metal is heated, for when steam is passed over red hot iron, hydrogen is produced, as follows:

$$3\,Fe + 4\,H_2O = Fe_3\,O_4 + 8\,H.$$

Not-metals do not generate hydrogen from water.

A better method for preparing hydrogen for laboratory use than by the action of metals on water is by that of the metals on acids, when hydrogen and a salt are formed, thus:—

$$Na + H\,Cl = Na\,Cl + H;*$$

but as action of sodium on hydrochloric acid is not practicably available it is necessary to substitute some other metal such as zinc or iron, when the chloride of the metal and hydrogen is formed, as follows:

$$Zn + 2\,H\,Cl = Zn\,Cl_2 + 2\,H$$

Zinc + Hydrochloric acid = Zinc chloride + Hydrogen.

$$Fe + 2\,H\,Cl = Fe\,Cl_2 + 2\,H$$

Iron + Hydrochloric acid = Ferrous chloride + Hydrogen.†

Instead of hydrochloric acid, dilute sulphuric acid could be used, thus:

$$Zn + H_2\,SO_4 = Zn\,SO_4 + 2\,H$$

Zinc + Sulphuric acid = Zinc sulphate + Hydrogen.

$$Fe + H_2\,SO_4 = Fe\,SO_4 + 2\,H$$

Iron + Sulphuric acid = Ferrous sulphate + Hydrogen.

The reaction between sodium or potassium and water does not differ in principle from those of zinc and iron on hydrochloric or sulphuric acid, for in either case, the metallic element hydrogen, was attached to a negative element or group of elements, thus:—

$$\overset{+}{H}\,(\overset{-}{OH}),$$

$$\overset{+}{H_2}\,(\overset{-}{SO_4})$$

$$\overset{+}{H}\,(\overset{-}{Cl})$$

and was displaced by another metal which possessed greater chemical energy in contrast with these negative groups. This is true of gas flame until red hot, turning out the flame and then instantly turning it on again. The platinum occludes the gases escaping from the burner, and, being warm, they unite with the oxygen of the atmosphere, so that the wire glows and finally sets fire to the gas. Occluded gases are frequently used in chemical operations.

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*This reaction can take place between sodium and gaseous H Cl. The solution of hydrochloric acid, which is the ordinary laboratory preparation, is not available for the purpose for the action is too violent.

†On comparing the formulæ of zinc chloride and ferrous chloride with those of zinc and ferrous hydroxides, the pupil will see that the metal combines with the same number of chlorine atoms as it does with hydroxyle groups.

Animals, when placed in an atmosphere of hydrogen, die of asphyxia, hydrogen not being poisonous, *per se*, as is proved by the fact that animals can live without discomfort in an atmosphere of hydrogen to which has been added a sufficient supply of oxygen; neither is hydrogen able to support combustion in the ordinary sense of the term, a burning candle becoming extinguished when placed in it. In order to be combustible in a gas a body must have a great tendency to unite with that gas; necessarily the substances which are ordinarily considered as combustible such as wood or a candle cannot burn in hydrogen, for they themselves are largely composed of hydrogen. Hydrogen burns quite readily in oxygen, with a very hot flame, and *vice versa*, oxygen will burn in hydrogen with the production of an equally hot flame; in both instances water is produced. (See page 21). Hydrogen will also burn in other gases for which it has a great affinity, in chlorine for instance, while the hydrogen compounds of the elements in which it burns will be produced.

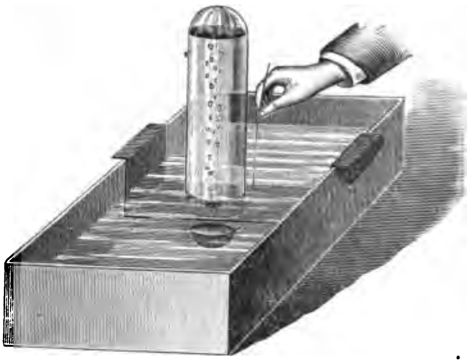
FIGURE 6.

In order to prove the formation of water by the combustion of hydrogen in the air, we have but to thoroughly dry the gas passing from a generator[17] and ignite the same at the tip of a burner[18] and then hold a cold glass jar over the same. Drops of water soon collect and run down the sides of the vessel. The hydrogen flame has a very high temperature and is very nearly not-luminous, but it can be changed to a luminous one by dropping a little powdered coal or lycopodium into it, for not-luminous flames are simply glowing gases, they are made luminous by glowing solids within them. Hydrogen, like other substances, burns more energetically in oxygen than in air, so that the temperature of a flame of hydrogen burning in the former is much higher than that of the same gas burning in the latter. This fact is taken advantage of in the use of the oxyhydrogen blow-pipe. This is an apparatus constructed as in Fig. (11) consisting of two concentric tubes drawn nearly to a point, through the outer one hydrogen is admitted and ignited, and then a stream of oxygen gas is passed through the central tube, thus mixing the two gases at their point of combustion. The most extreme heat of a flame of hydrogen burning in oxygen is thus obtained. The illuminating power of calcium lights is due to a piece of lime, an infusible substance, heated to incandescence by the oxyhydrogen blow pipe; zinc, iron, or tin burn readily in the flame, a piece of platinum wire is instantly melted; indeed, the fusing of platinum for the manufacture of various utensils is accomplished by this means.

CHAPTER IV.

WATER.

Symbol H_2O, *Specific gravity 1, Specific gravity of vapor, air = 1, is .62208, H = 2 is 17.89.*

When hydrogen is burned in oxygen, or oxygen in hydrogen, water is formed. The study of the composition of this substance and the methods by which this has been advanced, might serve as a type of all other similar investigations, so that for the purpose of becoming somewhat acquainted with the means of chemical research the subject will be discussed at some length. That hydrogen and oxygen, in uniting, form water is easily proved, but the question at once arises, is water alone produced or may not some other substance originate simultaneously when the combustion takes place? Indeed, when all of the products of combustion of hydrogen in the air are collected, an acid substance, nitric acid, is found to be produced. The formation of an acid by this means puzzled the original investigators, and not until they had exploded a mixture of pure hydrogen and pure oxygen, as Cavendish did in 1780, and so discovered that no acid whatever was produced under those circumstances, did they come to the conclusion that hydrogen and oxygen, in burning, formed water only. Another problem as regards water then presented itself. Before the last quarter of the eighteenth century it was generally supposed that water, by boiling, was changed to an earthy substance, for on boiling even pure distilled water in glass or earthen vessels an earthy residue remained after evaporation. Lavoisier took upon himself to prove that the universally accepted notion was erroneous. In order to do this he sealed some pure water in a glass flask, then weighed the same and heated through some weeks, when the total weight was unchanged. On evaporating the water, a solid substance remained, but then Lavoisier found that the flask had lost in weight, and this loss in weight was exactly equal to that of the earthy residue. As a consequence he came to the conclusion that the earthy substance, supposed to be formed by the boiling of water, was nothing more than a dissolved portion of the glass, deposited by evaporation. Scheele, at the same time, showed that this earthy residue had exactly the same composition as the glass in which the water had been boiled. Chemists had then proved two things by their investigations, that hydrogen and oxygen, in uniting formed nothing but water, and that this water, in evaporating, was volatilized unchanged. We have seen that water is decomposed by the electric current. It is not only necessary for the chemist to prove that hydrogen and oxygen are produced by this means; he must also show that nothing but these gases are formed. Sir Humphrey Davy noticed that, in electrolizing water, a certain amount of alkali separated at the negative pole, while acid was formed at the positive one. There were only three possible theories to hold; one was that these substances were produced from the water; the second, that they were formed by the decomposition of the glass, for glass is composed of an acid and an alkaline substance; and the third, that the surrounding air took part in the change. In order to discover the source of these impurities, Davy transferred the water to a gold vessel and then continued the process of electrolysis. Acid and alkali were formed as before, but the amount of alkali became less and less, until it finally disappeared, showing that this was due to a portion of the glass dissolved, while the production of acid continued. Davy came to the conclusion that this latter was due to nitric acid, produced from the atmosphere, and, as a consequence, the gold vessel was placed under a bell-jar on the receiver of an air pump, the air exhausted and replaced by pure hydrogen, when the formation of acid ceased. It was proved, therefore, that water changed to nothing but hydrogen and oxygen on electrolysis, and with that the chain of evidence was complete. There remained now to determine what proportionate volumes of hydrogen and oxygen were produced in the electrolysis of water, and what proportionate volumes united to form water. This matter had been in dispute for a number of years, until Gay Lussac and Humboldt showed that exactly twice as much hydrogen as oxygen, by volume, is contained in water,[19] in other words, for every two cubic centimeters of hydrogen there is one cubic centimeter of oxygen, and, if hydrogen and oxygen are mixed in exactly these proportions[20], the gas produced explodes violently when ignited by means of a taper or electric spark. If the exact mixture is exploded in a short heavy glass tube closed with mercury, over a trough filled with that metal, we would see that after the explosion the mercury would completely fill the tube, as the volume of water formed would be insignificant as compared to the volume of the gases used. The following facts have then been proved as regards water. It is composed of hydrogen and oxygen only; it decomposes into nothing but hydrogen and oxygen, and the volume of hydrogen is to the volume of oxygen as 2:1; furthermore, two volumes of hydrogen mixed with one of oxygen form an explosive mixture from which only water is produced, without a residue of hydrogen or oxygen.

Having proved the composition of water by volume, our next task is to discover the same by weight, and this was first most accurately determined by Dumas.* By passing pure hydrogen over heated copper oxide the following reaction takes place:—

$$\text{Cu O} + 2\text{ H} = \text{Cu} + \text{H}_2\text{O}.$$

Copper oxide + hydrogen = copper + water.

By this means we have a most ready method of discovering the proportional parts by weight in which hydrogen and oxygen unite. For, let us suppose the copper oxide to be perfectly dry and accurately weighed, then after the reaction the weight of the remaining copper subtracted from that of the copper oxide would give us the weight of oxygen which has gone to form water; if by some means we can collect the water formed and weigh the same with equal accuracy, by the difference in weight between that of the oxygen and of the total water we would have given the weight of hydrogen.

FIGURE 7.

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* Berzelius and Dulong first undertook to determine the quantitative composition of water by this method.

a = weight of copper oxide. c = weight of water formed.
b = weight of copper after the reaction. c — x = weight of hydrogen.
a — b = weight of oxygen = x and x:c — x will represent the ratio in which oxygen and hydrogen unite to form water.

This ratio was found by Dumas to be 1:7.98. Dumas took great care to purify the hydrogen which he used.[21] The water was collected by passing the gas through an empty glass flask in which the greater part was condensed, and then through a series of tubes filled with fused caustic potash and phosphorus pentoxide, which substances absorbed all of the remainder. The tubes are filled with perfectly dry and pure air before the operation and then weighed, after the water has been formed they are once more filled with dry and pure air and again weighed, when the gain in weight gives the amount of water formed. This latter, in 19 experiments was 945.439 grams, the loss in weight of the copper oxide, and consequently the amount of oxygen in the water was 840.161 grams leaving for hydrogen (945.439 — 840.161) or 105.278 grams. The ratio between hydrogen and oxygen, therefore is as 105.278: 840.16, or as 1: 7.98. Of late Morley, by using a different method, has proved that the ratio is more probably 1: 7.935.

The facts which we have discovered as regards water are then as follows:

It is decomposed into hydrogen and oxygen, and yields two volumes of hydrogen to one of oxygen; it is formed from two volumes of hydrogen and one of oxygen, and when the water so formed is heated above the boiling point, *i. e.*, measured as steam, it will be seen that 2 vols. of hydrogen + 1 vol. oxygen produce 2 vols. water vapor, and furthermore water contains the two elements in the proportional parts by weight of one of hydrogen to eight of oxygen. We shall subsequently see that in equal volumes of gases, under the same conditions of temperature and pressure, there are equal numbers of particles, so that if two volumes of hydrogen unite with one of oxygen to form water we are tolerably safe in assuming that two atoms of hydrogen unite with one of oxygen, and if we neglect the decimals, two parts by weight of hydrogen unite with sixteen of oxygen, from this it follows that in all probability, the atomic weight of oxygen is sixteen. This last conclusion cannot be absolutely certain, as we shall subsequently see, but we *are* sure that one part by weight of hydrogen unites with eight of oxygen to form water and formerly chemists were of the opinion that speculation should not extend beyond this certainty. They wrote the formula of water HO, meaning by this that hydrogen and oxygen united to form water in the proportion of one part by weight of hydrogen to eight of oxygen, and as eight parts by weight of oxygen were *equivalent* to one of hydrogen, eight was called the equivalent weight of oxygen; but as chemical and physical theory and investigation became more perfect, it was seen that we could form very definite conclusions as regards the atomic weights, so that equivalent weights were abandoned and our present atomic weights came into general use. The investigations on the composition of water will serve to illustrate the means by which our present chemical facts have become known, and the pupil should understand that when in the future the atomic weights of elements, or the formulæ of compounds are mentioned, these have been discovered by some equally painstaking means of investigation.

Water at ordinary temperatures is a nearly colorless liquid; when light is passed through a thick layer of the substance it will be seen to have a distinctly blue color. When heated above its boiling point, which with 760^{mm} pressure is at 100° centigrade, it is transformed into a colorless gas. When water is cooled, the substance contracts, following the general law; when heated, it expands. If however, water having a temperature above 4° centigrade is cooled, it will contract until that temperature is reached, and will then begin to expand until 0° centigrade, when it freezes. Water at 4° centigrade then has the greatest specific gravity,* so that any body of water on cooling toward that temperature will become specifically heavier; that portion on the surface, because it cools first, will sink, the warmer and lighter water below will rise and in this manner a continuous circulation will be kept up until the entire body has arrived at the temperature of 4° centigrade. Now the water on cooling further will expand, and hence the cooler portion will float on the surface until it arrives at 0°, when freezing begins and the crust of ice formed, floating on the surface, will act as a protection to the water below. As a consequence water freezes on the surface and not from below upward. In freezing, water expands, the specific gravity of ice being .9167; on cooling below its freezing point ice continuously contracts, following the usual law. The freezing point of water, or rather the melting point of ice, at standard atmospheric pressure is taken as 0° on the centigrade thermometer; this point is lowered by compression, so that ice at 0° centigrade can be fused by increasing the pressure; as soon as this is relieved the liquid instantly freezes. This fact can be experimentally proved by firmly pressing together two pieces of ice, when they will adhere as soon as this pressure is relieved.

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* If we place the density of water at 4° centigrade at 1. then water at 0° centigrade has a specific gravity of .99988.

Water is able to dissolve a large number of substances to form solutions. Solutions are homogeneous mixtures of two substances, either both or one of which must be gaseous or liquid. These mixtures cannot be separated by simple mechanical means. Gases can form these homogeneous mixtures in any proportion. When two substances are liquid the solution may take place in any proportion, as between alcohol and water, alcohol and ether, acetic acid and water; or one liquid, may partially dissolve another, as in the case of water and ether;* or lastly, one liquid may be entirely insoluble in another, as in the case of some oils and water. When a solid dissolves in a liquid, the latter is only able to take up a certain quantity, which, with any given liquid, varies with the nature of the solid. When the liquid has dissolved as much of the solid as it will, the solution is said to be saturated. As a rule, gases are less soluble in liquids the higher the temperature; they are therefore expelled from their solutions on heating. Solids, on the other hand are as a rule more soluble in hot liquids than in cold ones. As a consequence a saturated solution at the boiling point of the liquid will contain more of the dissolved solid than it will at a lower temperature, so that on cooling, a dissolved substance separates, frequently in a crystalline form. The process of dissolving crystalline solids in hot liquids and separating by cooling is called recrystallization, and is very frequently employed as a means of purifying crystalline substances. The solubility of solids in water varies very greatly; some substances are insoluble, others but very slightly so, so that the solution may be saturated when only a trace of dissolved substance is present, while again we have solids such as potassium hydrate and calcium or magnesium chloride which are soluble even in their own volume of water. The solutions formed are clear liquids which may have the color of the dissolved solid. In making solutions we frequently have marked changes of temperature. Where substances form no chemical union with water in dissolving, the temperature is lowered, for work must be done to change the crystallized solid to a liquid; thus potassium or ammonium nitrate on dissolving, cause a very marked lowering of the temperature.

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* In this latter case we can scarcely say that one liquid dissolves the other, for to take an example from the instance just cited, the other will dissolve just as much water as the water will dissolve ether.

Quite a number of substances can chemically unite with a certain number of molecules of water to form crystalline compounds in which the water is apparently not present as such, for the crystals are perfectly dry and have a definite form, the water being detected only on heating, when it passes off. Such combined water is known as water of crystallization; the number of molecules of water of crystallization and the crystalline form are always the same for any given compound, but in some few cases however a substance can crystallize in different forms, with different amounts of water of crystallization. To cite a few examples, copper sulphate crystallizes with five molecules of water as $Cu SO_4, 5 H_2 O$, ferrous sulphate with seven molecules as $Fe SO_4, 7 H_2 O$, sodium

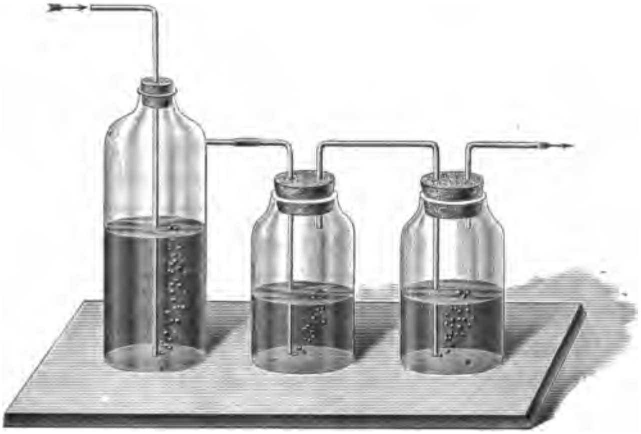
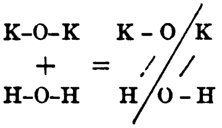


FIGURE 8.

carbonate with ten molecules, as $Na_2CO_3, 10H_2O$, and alum with twenty-four molecules as $Al_2K_2(SO_4)_4 + 24H_2O$. Substances which are chemically similarly constituted will frequently crystallize in the same, or at least in very similar crystalline forms; such substances are called isomorphous.* A number of compounds lose their water of crystallization on standing in the air, their crystalline form is destroyed and they finally disintegrate to form not-crystalline powders; such substances are efflorescent. On the other hand, we have a large number of bodies which are capable of taking up water from the atmosphere and dissolving in the moisture so concentrated; these are deliquescent. By far the greater number of substances are neither deliquescent nor efflorescent at ordinary temperatures but all substances with water of crystallization lose this at a comparatively moderate heat. When water of crystallization has been expelled from a substance the body is called anhydrous. Anhydrous salts dissolve in water with the evolution of heat; many, like calcium chloride, are able to absorb moisture readily, and as a consequence are most useful for drying gases. It must be borne in mind however that the majority of substances which crystallize do not contain water of crystallization.

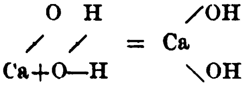
Water combines with many substances when it does not enter as water of crystallization; for example the oxides of the metals when soluble in water, unite with that substance to form the hydroxides.



or

$$K_2O + H_2O = 2KOH$$

Potassium Oxide + Water = Potassium hydroxide.



or

$$CaO + H_2O = Ca(OH)_2$$

Calcium Oxide + Water = Calcium hydroxide.†

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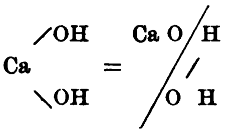
* The student should consult some elementary text-book in regard to the principles of crystallography. Isomorphous salts are, for instance,

$MgSO_4, 7H_2O$. $CaCO_3$,
$ZnSO_4, 7H_2O$. $SrCO_3$.

Two or more. substances are not truly isomorphous unless one can replace the other without altering the crystalline form, thus, $MgSO_4, 7H_2O$ and $ZnSO_4$ $7H_2O$, both crystallize in the rhombic system, and zinc can replace magnesium in crystals of $MgSO_4, 7H_2O$, without altering the crystalline form.

† Note again the difference between the formulae KOH and $Ca(OH)_2$. Here, we see, calcium has the power of retaining twice as many hydroxyle groups as did potassium, a relationship exactly similar to that of potassium and magnesium

In such cases the water entering into combination with the oxide is decomposed, it is no longer present as water but as hydroxyle to which group attention has already been called on page (28). The hydroxides, of course, differ most markedly in stability; some are very readily decomposed by heat into water and the oxide, while others, for example potassium hydroxide, can be fused at a high red heat without changing to the oxide. As a rule, the less pronouncedly metallic the element forming the hydroxide is, the more readily will that hydroxide be decomposed by heat. For example calcium hydroxide is decomposed as follows by heat:—



or

$$\mathrm{Ca\,(OH)_2} = \mathrm{Ca\,O} + \mathrm{H_2\,O}$$

Calcium hydroxyde = Calcium oxide + Water.

In the same way as water enters into combination with the oxides of the metals to form hydroxides, it can unite with the anhydrides of acids to form hydroxides called acids, to which attention will be called subsequently.

Pure water is very difficult to obtain owing to its great capacity for dissolving various substances. The impurities may be of two kinds, those mechanically suspended and those dissolved; while the dissolved impurities may be classed under three heads, gaseous, liquid and solid. The mechanically suspended impurities may be removed by filtration, that is, by passing the water through some porous substance such as unsized paper (so-called filter paper), or through unglazed porcelain. Those dissolved must be removed by distillation.* The gaseous impurities cannot all be eliminated by this means, for the oxygen and nitrogen of the atmosphere as well as the other impurities in the air are soluble in water, and will therefore be found in the distilled water. Liquid impurities may be removed by distillation, provided their boiling point is not too near

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hydroxides, and similar to the relationship in the formula of the chlorides $\mathrm{Ca\,Cl_2}$ $\mathrm{K\,Cl}$. If we were to call chlorine x, hydroxyle y, the relationship would become apparent in $\mathrm{Ca\,X_2}$, $\mathrm{Ca\,Y_2}$; Kx, Ky. These chemical changes are rendered more apparent if the pupil will take the trouble to write out the formulæ of reactions, atom for atom, as has been done above.

* Distillation is simply the process by which the steam of boiling water is collected in suitable vessels, and condensed to a liquid, For a description of the process of distillation any larger text book can be consulted.

that of water, where the boiling points of two liquids are within 10° of each other a complete separation by distillation is impossible. The solid impurities remain behind in the vessel from which water has been distilled. If distilled water is to be free from gases it must be boiled for some time in bottles and then hermetically sealed before allowing to cool.

All naturally occurring waters are more or less impure, the purest being rain-water and melted snow, but even these contain such solid and gaseous substances as they can collect in passing through the atmosphere. Rainwater in falling on the soil takes up such soluble substances as are contained therein, and in so doing is changed to spring-water. Of course, the dissolved impurities of spring-water vary greatly with the nature of the soil through which the water has passed; when the amount of dissolved impurity is not very great and is mainly calcium carbonate or sulphate, the water is fresh water, when quantities of salts are dissolved from the soil the water becomes a mineral water. Some springs are heated as they issue from the earth, these are called thermal springs. The most frequent salts in mineral waters are sodium and magnesium sulphates, sodium carbonate and carbonate of iron, while gaseous constituents like carbon dioxide and sulphuretted hydrogen are also met with. River water necessarily must contain the dissolved impurities which were in the springs from which the stream has its source, with some modifications introduced by the nature of the soil over which it has passed or by contaminations which have been introduced purposely or accidentally by decaying animal or vegetable substances. As streams pass through more or less thickly inhabited regions the proximity of dwellings and factories is apt to cause dangerous impurities in the water, for as a rule very little

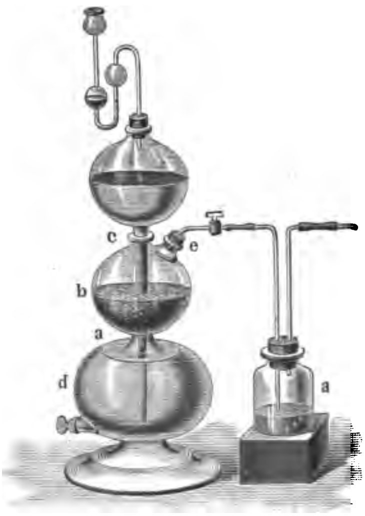

FIGURE 9.

care is exerted to keep sewage from reaching the same stream from which drinking water is taken. The water polluted will, on analysis, prove to contain compounds of nitrogen which have their origin in putrescent animal substances, the quantity of these compounds diminishes as the water is exposed to the oxidizing action of the atmosphere, yet, in the water thus purified by nature, there may be a large number of living micro-organisms which may cause disease, so that a drinking water should be examined not only with the purpose of ascertaining the quantity of decaying animal substance present, but also as to the number and kind of micro-organisms contained in it. Water may be contaminated by a considerable quantity of sewage and yet be harmless, for it may contain no harmful disease germs, while, on the other hand, water considered as chemically pure may be extremely dangerous by reason of germs contained therein.

In concluding the chapter on this most important subject, it is well to once more call attention to the extreme importance of thoroughly understanding the *changes of energy* which take place in the formation and decomposition of water. We must remember that hydrogen and oxygen (a metal and a not-metal) unite most readily, provided some impulse such as an electric spark or fire is added to a mixture of the gases, while, during the union, much heat was given off and, therefore, water possessed much less energy than did the elements hydrogen and oxygen; and the application of just as much kinetic energy, in some form, is necessary to decompose water as has been given off in its formation. When the energy is applied in the form of an electric current, two volumes of hydrogen and one of oxygen are produced.

We have, by this time, become somewhat more intimately acquainted with chemical equations. The pupil should practice writing the chemical equations which have been given, until he is entirely familiar with them, remembering, always, that the mere memorizing of such equations is useless, that the reasons *why* any reaction should take place, and *why* certain substances are formed from any reaction are of infinitely more importance than the equations, which, however, fix these reasons in the memory.

CHAPTER V.

OZONE AND HYDROGEN DIOXIDE.

When compared with the extraordinary chemical activity of oxygen at higher temperatures, the tendency of that element to unite with other substances under ordinary conditions is not very marked. Iron, copper and similar substances, which are oxidized when heated in the gas, remain unchanged in perfectly pure oxygen at ordinary temperatures, and we can readily see that, did oxygen possess the capability of oxidizing under those circumstances, there would result a complete alteration of the existing conditions upon the surface of the earth. The element is not, however, limited to the one form which we have discussed, it is also capable of existing in another character, in which its properties differ most remarkably from those of ordinary oxygen. An element capable of existing in two or more different physical and chemical forms is said to possess the property of allotropism; and the different modifications of the same element are called its allotropic forms. Oxygen, then, exists in two allotropic forms, oxygen and ozone—in the former one it has the properties which have already been described; in the latter, it possesses a marked odor, when large quantities are present it is irritating to the mucous membrane of the throat and nose and it is a most active oxidizer even at ordinary temperatures. We are only acquainted with ozone diluted with oxygen or air.

The fact that a room, in which a powerful generator of static electricity is in action, becomes filled with an odor resembling that of phosphorus has been known for some time, * while, in 1840, Schönbein found that the same odor was produced when moist phosphorus was exposed to the atmosphere.[22] The substance causing this odor was, at first, owing to its resemblance to chlorine, supposed to be an element, at a later date investigation seemed to show that it was simply an oxide of hydrogen differing from water, but de la

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* Since 1785, (Von Marum).

Rive showed that if oxygen, perfectly pure and dry, be passed through a narrow glass tube in which are inserted two platinum wires between which electric sparks are passing, a quantity of ozone is generated. This proved without a doubt that ozone was generated from oxygen alone, and subsequently the proof was brought that ozone on heating yielded nothing but oxygen.

Having discovered that ozone was simply oxygen in another form there remained to be decided whether in forming the former substance from the latter, any change in bulk of the gas occurred.

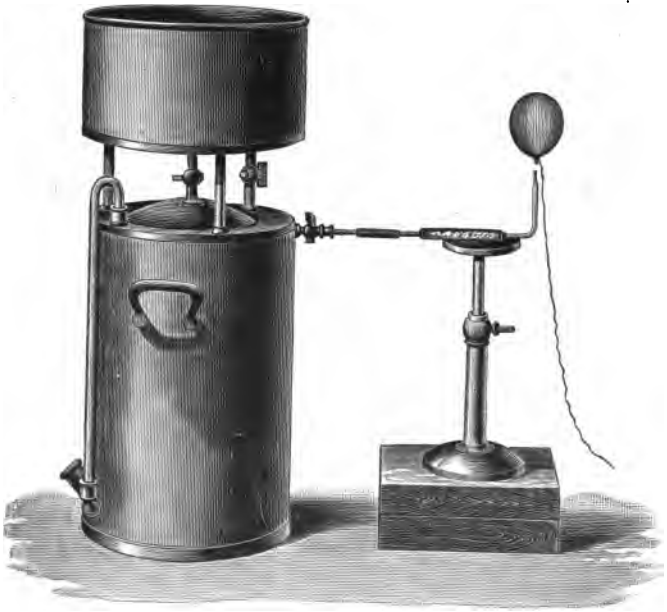

FIGURE 10.

Further study showed that a diminution in volume took place; and this contraction was such that from 3 c.c. of oxygen there resulted 2 c. c. of ozone, and conversely from two of ozone there resulted three of oxygen. We have learned that in equal volumes of gases there are equal numbers of particles, it follows that if we were able to obtain pure ozone, there would be as many particles of ozone in a given volume as there would be of oxygen. Now, we have seen that in the formation of ozone, oxygen contracts from 3 volumes to

2, it follows that a given *weight* of ozone occupies only two-thirds the volume of the same weight of oxygen, hence, the weights of equal volumes of oxygen and ozone must be to each other as 2:3; and hence, if there are the same number of particles in each gas, the weight of a molecule of oxygen must be to that of ozone as 2:3. We will learn, empirically for the present, that the molecule of oxygen is composed of two atoms, and that its molecular weight being the sum of the atomic weights of the atoms composing the molecule must be 32, it follows that the molecular weight of ozone is 48, and that if ordinary oxygen has a molecule composed of two atoms of oxygen, ozone must have one consisting of three. In this case then the cause of allotropism is evidently in the different molecular structure of the two modifications of the same element, and from this the student will see that a change in the molecule brings with it a change in the character of the substance, regardless whether that molecule is composed of atoms of the same kind or of those of different kinds. The two reactions,

$S + O_2 = S\,O_2$, Sulphur dioxide,

$O + O_2 = O\,O_2$ Ozone,

will serve to make this meaning more clear. By oxidizing sulphur we obtain sulphur dioxide, a body differing in properties from both sulphur and oxygen, by oxidizing oxygen we obtain ozone, a body differing in properties from oxygen, but not perhaps as markedly as sulphur dioxide does from sulphur. The addition of energy was necessary to form ozone from oxygen, it is an endothermic compound, and hence has a great tendency to break down with the evolution of heat. The fact that it can oxidize metals under ordinary conditions has already been alluded to;* it also can oxidize a great many organic substances, such as albumen, milk, shavings, corks or india rubber; if such substances are placed in oxygen containing ozone the odor of the latter disappears at once. As ozone is formed in a great variety of ways, for instance by the evaporation of liquids or by discharges of electricity, it follows that more or less of the substance must occur in the atmosphere at times but, owing to the presence of oxidizable substances, we would scarcely expect any quantities of ozone in the atmosphere of cities. Large quantities of ozone would undoubtedly be harmful if inhaled; small quantities have never been proved to have any effect.

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* Some pure and bright mercury shaken with gas which contains even traces of ozone is instantly oxidized, the mercury adhering to the sides of the flask.

Ozone is a gas which has a blue tint, as can be seen by looking in the direction of a white paper through a long tube containing ozone. If it could be obtained pure it would undoubtedly be easily condensed to a liquid, for, although it is always greatly diluted with oxygen, it forms an indigo-blue liquid at temperatures above those required to liquify oxygen.[23]

Hydrogen and oxygen form two distinct compounds, in one of which, water, we have two parts by weight of hydrogen united to sixteen of oxygen; in the other, two of hydrogen to thirty-two of oxygen; the existence of these two compounds being an excellent example of the law of multiple proportions. We have already decided that the formula of water is H_2O, and hence we must assign the formula H_2O_2 to hydrogen dioxide, remembering that as we have not been able to obtain this substance in the form of a gas, H_2O_2 only can represent the formula weight; the molecular weight may be any multiple of this formula weight, or ($n\ H_2O_2$).

Hydrogen dioxide is prepared by adding a dilute acid, preferably sulphuric acid, to barium dioxide.

$$\underset{\text{Barium dioxide}}{Ba\,O_2} + \underset{\text{Sulphuric acid}}{H_2\,SO_4} = \underset{\text{Barium sulphate}}{Ba\,SO_4} + \underset{\text{Hydrogen dioxide.}}{H_2\,O_2,}$$

The barium sulphate formed is insoluble in water,[24] it can therefore be allowed to settle to the bottom of the vessel in which the peroxide of hydrogen is prepared and the clear supernatent liquid then poured off; by allowing the excess of water to evaporate[25] there remains a very concentrated solution of hydrogen dioxide having a specific gravity of 1.45, and which does not freeze at — 30°. The concentrated solution must be preserved in ice, for on warming to ordinary temperatures a rapid evolution of oxygen takes place, and nothing but water remains—a too rapid heating of the liquid to the boiling point of water will cause it to explode. Dilute solutions of the dioxide have a bitter taste.

Hydrogen dioxide owes its chief value to the readiness with which it yields its oxygen, resembling ozone in that particular; indeed, the most delicate test for both is the same and owes its value to their oxidizing power. Hydrogen dioxide when added to a solution of potassium iodide yields iodine:

$H_2O_2 + 2\,KI = 2\,K\,OH + 2\,I.$

Hydrogen dioxide + Potassium iodide = Potassium hydroxide + Iodine.

$O_3 + 2\,KI + H_2O = 2\,K\,OH + O_2 + 2\,I$

Ozone + Potassium iodide + Water = Potassium hydroxide + Oxygen + Iodine.

In the latter case the addition of water is necessary, in the former a compound of hydrogen and oxygen which yields water is already present, but in both cases the oxygen given off changes the iodide to the hydroxide of potassium. Iodine has the power of turning starch paste to a deep blue color, so that the addition of some of this substance will render even minute traces of iodine visible.

Both ozone and hydrogen dioxide owe their peculiar powers of oxidation to the fact that they can yield oxygen in a condition known as the nascent state. Oxygen, as well as a number of other elements, exists as molecules, each molecule being formed of two atoms. A considerable amount of energy is necessary to decompose these molecules; indeed, in the case of hydrogen for instance, it is doubtful whether any heat which we can command will be able to decompose the molecules of hydrogen into atoms. As a consequence it follows that the individual atoms possess much more chemical energy than do the molecules and hence must tend to unite with some other atom or with some molecule. When an element is liberated from any of its compounds it must exist as individual atoms, which however instantly unite to form molecules. If however any substance is present on which the atoms can act they will then react with that substance. It follows therefore, that elements are chemically most active at the very moment of their liberation from compounds (*in statu nascendi*). If we pass hydrogen gas through nitric acid no change will take place, no matter how long we may continue

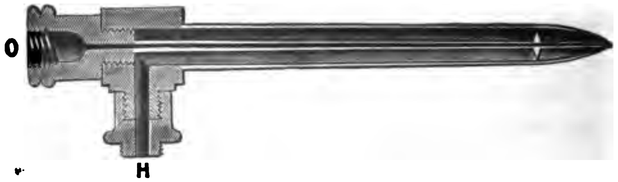

FIGURE II.

the operation, but if we generate hydrogen within the acid, as for instance by placing a piece of zinc in nitric acid, the hydrogen will rob the nitric acid of its oxygen, forming water and an oxide of nitrogen containing less oxygen than does nitric acid. Instances of the action of elements in the nascent state are extremely numerous, but we are even aware of a number of cases where compounds are more energetic, chemically, at the moment of their formation than at any other time, and in such cases this explanation of the nascent state is inadequate. The compound CO, carbon monoxide, can act, under certain conditions, as if it were in the nascent state but we have no reason to suppose that this compound ever exists otherwise than as the molecule represented by the formula CO. The above explanation of the nascent state, if correct, is probably applicable only in a limited number of cases. The fact remains however, that elements frequently enter into reaction at the moment of their liberation from compounds, where they would be entirely indifferent under other circumstances. Oxygen in the nascent state is liberated by hydrogen dioxide and by ozone, for ozone $\begin{array}{c}O\\ \vert\\ O\end{array}\!>O$, O_3, breaks down into one molecule of oxygen and an atom of the same element $\begin{array}{c}O\\ \vert\\ O\end{array}\!>O = \begin{array}{c}O\\ \vert\\ O\end{array} + O$ and hydrogen dioxide into water and an atom of oxygen $\begin{array}{c}H\text{–}O\\ \vert\\ H\text{–}O\end{array} = \begin{array}{c}H\\ \\ H\end{array}\!>O + O$, and as a consequence both of these substances are powerful oxidizers and bleachers. The tendency of oxygen when liberated from ozone to unite with other atoms is so great that it can even take oxygen away from other compounds to form a molecule of oxygen; for instance, when brought in contact with silver oxide the following reaction takes place—

$$Ag_2O + O = 2\,Ag + O_2$$

and similar reactions take place with hydrogen dioxide.

CHAPTER VI.

THE HALOGENES.

We have now studied a metal, a typical not-metal and the product formed by the union of the two and having gained an insight into quite a number of chemical reactions as well as into the mode of action of the molecules and atoms, we will now go to the discussion of the elements by families, taking them up in the natural order assigned to them by their atomic weights, remembering that as was said in the introduction, the properties of the various elements are given by their atomic weights. The first group of elements which we will study are the most not-metallic in their characteristics, and the plan will be to work from this family through such with a diminishing not-metallic character until finally we arrive at groups composed entirely of the metals.

The Halogenes (salt producers) consist of four elements:

Fluorine,	atomic	weight	19.
Chlorine,	"	"	35.45
Bromine,	"	"	79.95
Iodine,	"	"	126.85

With increasing atomic weight we have a *decrease* in the not-metallic properties of the elements composing such a family and this change is well shown in the decreasing stability of the compounds of the halogenes with the metals. If we examine their hydrogen compounds, which are formed by the union of one atom of hydrogen with one of the halogene, (HF, HCl, HBr, HI) we are at once impressed by this change—for hydroiodic acid (HI) decomposes most readily upon heating, a hot wire introduced into the gas will change it to hydrogen and iodine; hydrobromic acid, $H\,Br$, is less readily separated into its elements; hydrochloric acid ($H\,Cl$) is broken down, if at all, only by the application of a very great amount of heat and we have so far as we know never effected a decomposition of hydrofluoric acid by heat alone. We can see this same difference illustrated by bringing chlorine into a solution containing sodium bromide or iodide; the chlorine will at once form sodium chloride, liberating bromine or iodine; while bromine, added to a solution of sodium iodide, will set iodine free, and fluorine would without doubt decompose the compounds of any of the other halogenes with the metals. This difference in the character of the halogenes is shown by the heat of formation of the hydrogen compounds given in the table at the end of the chapter. With increasing atomic weight we necessarily have changes in the physical properties of the elements. Fluorine is a colorless gas, chlorine a yellowish-green gas, rather easily converted to a liquid, bromine is a dark brown liquid at ordinary temperatures, while iodine is a solid of almost metallic appearance. The halogenes all have a peculiar odor and attack the skin and mucous membrane. Other points of resemblance will become apparent in the detailed study of the elements. They all, with the exception of fluorine and bromine, form oxides, and all but fluorine, acids with oxygen and hydrogen a study of which will be deferred until a subsequent chapter is reached. The halogenes themselves are never found as free elements, but occur united to some metal, as the fluoride, chloride, bromide or iodide. The metals most frequently found united with the halogenes are sodium, potassium, magnesium, or calcium, so that for instance, sodium chloride, (common salt) is the most frequently occurring compound of chlorine. Having given a few of these general characteristics, we will go to the study of the individual elements.

CHAPTER VII.

FLUORINE AND HYDROFLUORIC ACID.

Symbol F, atomic weight, 19. Symbol HF, specific gravity of liquid .9879; of gas, air = 1 is 1.364; H = 2 is 39.32, the molecule is $H_2 F_2$.

This element chiefly occurs in nature combined with the metal calcium as fluorspar, (Fluorite, $Ca F_2$), a crystalline mineral quite frequent of occurrence; in addition to this, cryolite, a fluoride of sodium and aluminum, ($Al F_3$, 3 $Na F$) occurs in large masses in Greenland, and is a considerable source of fluorine compounds; while small quantities of fluorides occur in the enamel of teeth and blood, and traces of the same are found in sea water.

Fluorine has until recently resisted all attempts to isolate it because of its great chemical affinity for other elements, be they metal or not-metal, so that it would combine with other substances as soon as liberated from its compounds. Quite recently a French chemist, Moissan, succeeded in preparing the element by electrolysis of perfectly pure liquid hydrofluoric acid placed in a U shaped platinum tube and cooled to a low temperature.* When the electric current passes through hydrofluoric acid the latter is decomposed into hydrogen and fluorine, just as we decompose water into hydrogen and oxygen, the hydrogen separating at the negative pole, the fluorine at the positive.

The element is a colorless gas, which does not attack platinum but instantly unites with elements such as silicon, boron, arsenic, sulphur, iodine, iron; organic substances, such as corks, petroleum, etc. The substances so attacked take fire in the gas so that all the phenomena of combustion in oxygen are repeated with fluorine in a more violent degree and under ordinary conditions. If the gas is passed into water, the latter is instantly decomposed, forming ozone and hydrofluoric acid, a reaction which is very interesting; for the power of decomposing water which members of the halogene family possess, diminishes with increasing atomic weight. The reaction is as follows:—

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* By liquid methylchloride, boiling point —22.5°.

$$2\,F + H_2O = 2\,HF + O.$$

Fluorine + Water = Hydrofluoric acid and Oxygen.

The atoms of nascent oxygen then can combine with each other to form ozone.

The compound of hydrogen and fluorine, hydrofluoric acid, was first identified as a peculiar acid by Scheele (1771), although the fact that a substance which would attack glass could be produced by the action of sulphuric acid on fluorspar had been known for some time (1670). The nature of hydrofluoric acid was misunderstood for some time, owing to the opinion formerly held by chemists that all acids must contain oxygen, so that the existence of oxygen was presupposed in hydrofluoric acid. We now know that no compounds of fluorine and oxygen exist.

Hydrofluoric acid can, as we have seen, be produced by the action of fluorine on water and by direct union of hydrogen and fluorine, just as water was formed by direct union of hydrogen and oxygen, and so great is the tendency to form this compound that fluorine will take hydrogen away, possibly, from any other compound containing that substance. To prepare hydrofluoric acid for the laboratory or for commercial purposes, other less expensive means

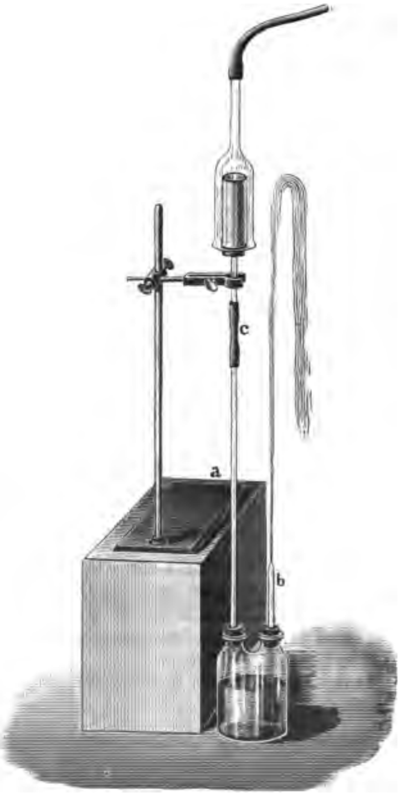

FIGURE 12.

are resorted to. If a fluoride, such as sodium fluoride or calcium fluoride is treated with sulphuric acid, the following reaction takes place:*

$$2\,NaF + H_2SO_4 = Na_2SO_4 + 2\,HF$$

Sodium fluoride + Sulphuric acid = Sodium Sulphate + Hydrofluoric acid.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2\,HF$$

Calcium fluoride + Sulphuric acid = Calcium Sulphate + Hydrofluoric acid.

Reactions such as the above are very frequently met with; the hydrogen of the acid simply exchanging places with the metal of the salt to form a new salt and a new acid. Such reactions are designated as double decompositions, and as a practical hint we can say that they take place when an insoluble or a volatile substance can be produced.† We will inquire more closely into the nature of double decompositions when we have studied a larger number of chemical reactions. The method given above is one very frequently employed in the preparation of the various acids from their salts.

Hydrofluoric acid is a colorless mobile liquid which freezes at —102°, boils at +19°, (about the temperature of a warm room) and which fumes strongly in the air because of its attraction for moisture. The vapor of hydrofluoric acid is very irritating even when inhaled in small quantities, while any considerable amount can cause death. A drop of the acid put on the hand causes a most painful blister which ultimately changes to a slowly healing ulcer, so that great care must be exercised in handling this acid. The usual commercial acid is a solution of hydrofluoric acid in water. It is a colorless, extremely acid liquid, fuming in the air, and is transported in bottles made either of paraffine or of guttapercha, for the acid readily attacks glass.

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*As hydrofluoric acid attacks glass the pure substance must be prepared in platinum vessels.

† Hydrofluoric acid is a volatile substance.

CHAPTER VIII.

CHLORINE.

Symbol Cl, atomic weight 35.45, specific gravity, air = 1 is 2.45, H = 2 is 70.5. 1 c.c. weighs .003173 grams.

Chlorine occurs in nature combined with various metals as chlorides, never as the free element. The most important chloride is that of sodium ($Na\,Cl$, sodium chloride,) or common salt. This substance forms the major portion of the solid residue left upon evaporation of sea-water and is consequently the larger part of the salt beds of marine origin and of those composed of rock salt. In less quantity chlorine occurs combined with potassium as the mineral sylvin ($K\,Cl$, potassium chloride) or as a chloride of magnesium and of potassium ($K\,Cl, Mg\,Cl_2 + 6\,H_2\,O$, carnallite); the chlorides of iron, lead, silver, etc., occur in small quantities, while chlorides are found in the ashes of plants and in animals.

The element was not discovered until 1774, at the beginning of the period in which were made the great advances in chemistry recorded in the introduction; the first chemist to prepare chlorine being Scheele. He called it dephlogisticated muriatic acid, for it was muriatic acid from which phlogiston (hydrogen) had been extracted. Chlorine was for some time supposed to be a compound of oxygen with an unknown element called murium; Sir Humphrey Davy first definitely asserted that chlorine was an element, calling the element chlorine from χλωρὸς, greenish yellow, the gas having that color.

Evidently, in order to prepare chlorine, our method must be to remove the metal from some chloride; hydrogen chloride (hydrochloric acid,) being the chloride easiest available. If we subject a concentrated solution of hydrochloric acid to the action of an electric current,[26] we will decompose the substance in exactly the same manner as we did hydrofluoric acid, with the exception that we can readily perform the operation in glass vessels which are not attacked by chlorine as the chemical energy displayed by chlorine is not as great as that of fluorine. We can also remove hydrogen from hydrochloric acid by other means; for instance by some oxidizing agent, when water and chlorine are produced, as follows:

$$2\,HCl + O = H_2O + 2\,Cl.$$

Hydrochloric acid + Oxygen = Water + Chlorine.

The oxygen of the atmosphere can accomplish this under proper conditions, and a process of commercial preparation of chlorine* has its origin in this fact. If a mixture of hydrochloric acid and oxygen is passed through a heated tube in which are placed pieces of porcelain or fire-brick saturated with a solution of copper sulphate, chlorine and water are formed. The copper sulphate remains unchanged at the end of the reaction so that the reason for its peculiar action is not understood.

Manganese dioxide is the most convenient oxidizer for the preparation of chlorine, when it is brought in contact with hydrochloric acid, the following reaction takes place:[27]

$$1.\ Mn\,O_2 + 4\,H\,Cl = Mn\,Cl_2 + 2H_2O + 2\,Cl$$

Manganese dioxide + hydrochloric acid = Manganous chloride + Water + Chlorine.

The manganese dioxide furnishes the oxygen which changes the hydrogen of hydrochloric acid to water, and at the same time in all probability a chloride of manganese is formed, having four atoms of chlorine in the formula weight, thus:

$$2.\quad Mn\,O_2 + 4\,H\,Cl = Mn\,Cl_4 + 2\,H_2\,O.$$

This chloride is however very unstable and breaks down into manganous chloride and chlorine, as follows:

$$3.\quad Mn\,Cl_4 = Mn\,Cl_2 + 2\,Cl,$$

so that combining equations 2 and 3, we obtain equation 1. As a rule, chemical equations are expected only to represent the ultimate products of any chemical reaction, as does equation 1, but if we wish to thoroughly understand chemical changes it is necessary to inquire into all of the various stages of chemical reactions. Other oxidizing agents, as well as manganese dioxide, † are capable of furnishing oxygen to form water and chlorine.

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* Deacon's process.

† Such oxidizing agents are potassium permanganate ($K\,Mn\,O_4$), potassium bichromate ($K_2\,Cr_2\,O_7$) Nitric acid (HNO_3), etc. In all of these cases the principle is the same, the sole object being to remove hydrogen from hydrochloric acid, forming chlorine and water. Manganese dioxide is employed because it is cheap.

A mixture of common salt ($NaCl$, sodium chloride) and sulphuric acid yields hydrochloric acid, so that it is often convenient to prepare chlorine by mixing sodium chloride and manganese dioxide in a flask and then adding sulphuric acid. In this case it must be remembered that the $MnCl_2$ (manganous chloride) formed, would also be acted upon by the sulphuric acid, forming manganous sulphate and hydrochloric acid, which would further be converted by the manganese dioxide as follows:

$$MnCl_2 + H_2SO_4 = MnSO_4 + 2\,HCl;$$
$$MnO_2 + 2\,H_2SO_4 + MnCl_2 = 2\,MnSO_4 + 2\,H_2O + 2\,Cl;$$

or when the usual mixture of sodium chloride and manganese dioxide is used:

$$MnO_2 + 2\,NaCl + 2\,H_2SO_4 = MnSO_4 + Na_2SO_4 + 2\,H_2O + 2\,Cl.$$

In all cases the principle of the reaction is the one given on the previous page, the sodium chloride serving simply to furnish hydrochloric acid.

Several other methods for the preparation of chlorine have been devised some of which are of commercial value, as for instance the preparation by heating magnesium chloride in a current of air, the reaction resembling that of the action of oxygen on hydrochloric acid:

$$\underset{\text{Magnesium Chloride}}{MgCl_2} + \underset{\text{Oxygen}}{O} = \underset{\text{Magnesium Oxide}}{MgO} + \underset{\text{Chlorine.}}{2\,Cl}$$

The magnesium oxide formed can be dissolved in hydrochloric acid, once more forming magnesium chloride and thus the process can be continued without serious loss of magnesium.

Chlorine, at ordinary temperatures, is a greenish yellow gas the color of which becomes darker upon heating. It has a peculiar, irritating odor which must be tested only when the gas is very dilute, for any great quantity of the gas entirely destroys the sense of smell, causing inflammation of the mucous membrane of the throat and lungs, coughing and hæmorrhages, while an annoying catarrh follows its inhalation so that great care must be exercised in working with the gas. A pressure of six atmospheres at 0° condenses chlorine to a liquid, at ordinary atmospheric pressure it becomes liquid at—35° and freezes at—102°, its specific gravity, air being one, is 2.49 at temperatures up to 1200°,* at higher temperatures the specific gravity becomes less, being but 2.02 at 1400°, thus showing that the chlorine molecules begin to decompose into the individual atoms at about white heat. This decomposition of molecules into simpler ones or into atoms is called dissociation, the temperature of dissociation varying with different substances according to the amount of heat given off in their formation; it of course being necessary to add as much energy in the decomposition of a substance as was given off in its formation. At very high temperatures, such as exist in the chromosphere of the sun, dissociation of all complex substances is complete, so that no chemical compound is possible.

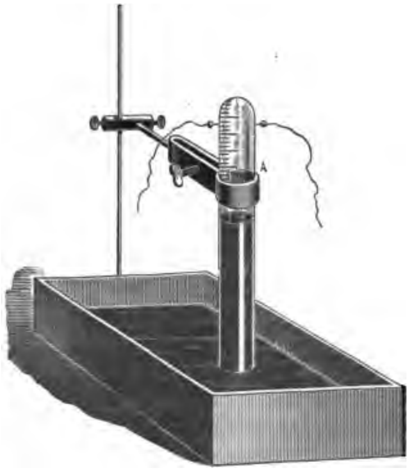

FIGURE 13.

Chlorine is tolerably soluble in water, one volume of that substance absorbing 2.5 volumes of chlorine at ordinary temperatures. The solution of the gas so produced, known as chlorine water, has the odor of chlorine and the properties of the gas. When chlorine water is cooled to near the temperature of freezing water it is changed to a transparent crystalline substance (chlorine hydrate,† having the composition $2\ Cl + 8\ H_2O$,) which slowly gives off chlorine at low temperatures and rapidly upon heating, so that if chlorine hydrate crystals be placed in one end of a bent glass tube as shown in Fig. 17 while the other end is cooled by snow and salt, and the crystals are then gently warmed, chlorine will condense to a liquid in the cold part of the tube.

Chemically, chlorine greatly resembles oxygen, with this distinction; while oxygen under ordinary circumstances is chemically inactive, chlorine at ordinary temperatures unites with many ele-

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[*] This, H = 2 would give a specific gravity of 71.88, the atomic weight of chlorine is 35.45, which would give a molecular weight of $Cl_2 = 70.90$, hence below 1200° chlorine molecules consist of two atoms to the molecule.

[†] Prepared by passing chlorine into ice water.

ments, metallic or not-metallic, forming chlorides the formulæ of which bear a great resemblance to the corresponding oxides; thus we have:

$P_2 O_5$	$P Cl_5$	$Al_2 O_3$	$Al Cl_3$
Phosphorus pentoxide.	**Phosphorus pentachloride.**	**Aluminium oxide.**	**Aluminium chloride**

$P_2 O_3$, phosphorus trioxide. $P Cl_3$, phosphorus trichloride.

The difference between the formulæ of chlorides and oxides, as seen from the above, is that in the oxide one-half as many atoms of oxygen unite with one atom of the other element entering into the compound as do chlorine atoms in the chloride; this relationship becomes clearer if we double the formulæ of the chlorides for purposes of comparison:

$$P_2 O_5, \quad P_2 Cl_{10}$$
$$P_2 O_3, \quad P_2 Cl_6.$$

One oxygen atom is therefore capable of taking the place of *two* chlorine atoms in chemical compounds and in writing chemical formulæ this difference must always be born in mind. What is true of chlorine applies to the other halogenes as well.

Phosphorus which has previously been ignited in the air will continue to burn in an atmosphere of chlorine, with a pale, greenish flame:

$$P + 3 Cl = P Cl_3, \text{ Phosphorus trichloride.}$$

Pronounced metals such as sodium, when heated to their kindling temperature, will burn in chlorine gas,

$$Na + Cl = Na Cl, \text{ sodium chloride.}$$

Carbon when heated in the presence of chlorine will form the chloride of that element:

$$C + 4 Cl = C Cl_4, \text{ carbon tetrachloride.}^*$$

Chlorine unites with hydrogen so very readily that it will even extract hydrogen from its numerous compounds with carbon. A piece of filter paper saturated with turpentine and placed in chlorine gas will take fire, sometimes with explosive violence, forming hydrochloric acid and separating in the form of soot the carbon which was in the turpentine.[†] But it is not only from compounds of carbon that chlorine will extract hydrogen, it will do so from a multi-

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[*] The pupil will note that in this formula two chlorine atoms take the place of one oxygen atom, as will be seen from the formulæ $C Cl_4$, CO_2.

[†] Turpentine is a compound of carbon and hydrogen.

tude of other substances containing that element, as from sulphuretted hydrogen, (H_2S) ammonia (NH_3) or even from water, in each case forming hydrochloric acid and liberating the element previously combined with hydrogen:

$$H_2S + 2\,Cl = 2\,H\,Cl + S,$$

Hydrogen sulphide + chlorine = hydrochloric acid + sulphur.

$$NH_3 + 3\,Cl = 3\,H\,Cl + N,$$

Ammonia + chlorine = hydrochloric acid and nitrogen,

$$H_2O + 2\,Cl = 2\,H\,Cl + O.$$

Water + chlorine = hydrochloric acid + oxygen.

The cause for these reactions in each case is that in contact with hydrogen, chlorine possesses greater chemical energy than the other elements. This is shown by the fact that hydrochloric acid, when dissolved in water, has a greater heat of formation than water, sulphuretted hydrogren or ammonia.

Thus, NH_3 formed from its elements gives 204 K,*
H_2S " " " " " 73 K,
H_2O " " " " " 684 K,
$2\,H\,Cl$ " " " " " 786 K.

Chlorine water placed in the sunlight will form hydrochloric acid and liberate oxygen; but chlorine and water can yield oxygen and form hydrochloric acid even without the aid of sunlight, provided some substance is present which can be oxidized. It is to this property that chlorine owes its commercial value, its chief industrial use being as a bleaching agent, its power of bleaching depending, at least in the great majority of cases, upon its capability of liberating nascent oxygen from water. That this is the case can be proven by placing a piece of colored calico in a jar of dry chlorine, no bleaching will take place until water is added and then the bleaching action of chlorine at once becomes apparent.[28] Chlorine is very frequently employed as an oxidizing agent in laboratory work; an oxidizing agent being a body which can chemically furnish oxygen, either *per se* or by the decomposition of some oxide.

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* K stands for the quantity of heat which a gram of water loses when cooled from 100° 0°. In speaking of heats of formation or of reactions, the quantities of substances reacting are as many grams as are expressed by the atomic or formula weights. Thus when we say the heat of formation of H_2O is 680 K, we mean that two grams of hydrogen uniting with sixteen of oxygen give 680 K. By heat of solution we mean the heat given off by dissolving the formula weight of a substance in grams in an unlimited quantity of water. Thus "the heat of solution of hydrochloric acid is 172 K" means that 36.45 grams H Cl give off 173 K while dissolving in an unlimited amount of water.

CHAPTER IX.

HYDROCHLORIC ACID.

Symbol, HCl, Specific gravity, air = 1, is 1.2596, H = 2, is 36.5, 1 cc. at 0° and .76 m. weighs .0016278 grams.

Hydrochloric acid occurs only very rarely in nature in the exhalations of some volcanoes and in the springs arising from the craters; for instance the Rio Vinagre, arising in the Andes, contains .08 per cent., the Paramo de Ruiz, in New Granada .8 per cent. of free hydrochloric acid.

The aqueous solution of the acid was first prepared by Basil Valentine in the 15th century by distillation of salt (NaCl, sodium chloride) with ordinary green vitriol ($Fe\,SO_4$, ferrous sulphate); it was subsequently investigated by a number of alchemists, but the pure gas was not obtained until 1772 when Priestly made pure hydrochloric acid. The old name was spiritus salis or acidum muriaticum (from Murias, Sea salt) and at the present day the aqueous acid is frequently called muriatic acid. When first investigated, hydrochloric acid was supposed to contain oxygen, but Davy in 1810 proved that it was composed of nothing but hydrogen and chlorine.

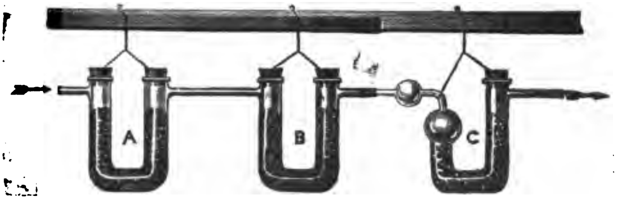

FIGURE 14.

The acid is best prepared by treating the chloride of a metal, preferably sodium chloride, with sulphuric acid, when the following reaction takes place:

$$2\,Na\,Cl \;+\; H_2\,SO_4 \;=\; Na_2\,SO_4 \;+\; 2\,H\,Cl,$$

Sodium chloride + Hydrogen sulphate = Sodium sulphate + Hydrogen chloride,

The gas can be collected over mercury or, being heavier than air, by downward displacement, but not over water as it is extremely soluble in that substance. Hydrochloric acid is a colorless gas with an acid odor, it fumes strongly in the air owing to the condensation of moisture from the atmosphere; it cannot be breathed, as it causes violent coughing; it is neither combustible, nor will other substances burn in it. The stability of union of hydrogen and chlorine is very great, at about 1800° (high white heat) hydrochloric acid begins to slightly decompose into hydrogen and chlorine, but as we have learned the great tendency which hydrogen has to unite with chlorine, this stability is not unexpected. Hydrochloric acid is very soluble in water; at 0° one volume of water will dissolve 505 volumes of hydrochloric acid gas, the solution then contains 43 per cent. of the acid.[30]

When chlorine is brought in contact with hydrogen, in the dark, no reaction takes place; if the mixture of the two gases be exposed to the sunlight, or if a lighted taper is applied or an electric spark allowed to pass through the gases, a violent explosion takes place and hydrochloric acid is produced. On the other hand if a current of electricity is passed through hydrochloric acid[31] the chlorine will separate at the positive pole, the hydrogen at the negative; this resembles the decomposition of water, excepting that with hydrochloric acid equal volumes of hydrogen and chlorine are produced, while in the case of water two volumes of hydrogen and one of oxygen result. When hydrogen and chlorine are mixed in equal volumes and then exploded, there is no change in volume, while the mixture of gases is entirely converted into hydrochloric acid; furthermore, sodium when it is placed in a closed volume of hydrochloric acid, will absorb the chlorine (forming $NaCl$, sodium chloride) and the volume of the gas will be diminished by one-half.[32]

We have now proved that hydrochloric acid decomposes into equal volumes of hydrogen and chlorine and that equal volumes of hydrogen and chlorine unite to form hydrochloric acid without change of volume. The relationship in the volumes of hydrogen and oxygen producing water was equally simple, so indeed is that between the volumes of any gases uniting to form a gaseous compound, so that Gay Lussac, who first accurately investigated the subject, was able to formulate the following law:

"If gaseous substances enter into chemical combination, their volumes are in simple ratio to each other, and if a gaseous substance is formed by their union, its volume also is in simple ratio to the volume of the original gases."

According to the kinetic theory of the nature of gases, now universally held, these substances are composed of particles of matter which are flying about in right lines until they impinge on the sides of the vessel in which the gas is contained or on each other, when, being perfectly elastic, they rebound. The particles of the gas are separated by such distances that their own volume exercises no influence on the volume of the gas as a whole. Now, the weight of a given volume of gas is but the sum of the weights of the individual particles making up that gas and the specific gravity of any gas, if air is taken as unity, is equal to the weight of a given volume of that gas as compared with that of the same volume of air. Investigation has shown us that the ratios between the specific gravities of elementary gases and those between their combining weights bear a simple relationship to each other, thus the specific gravity of hydrogen in round numbers is .07, of oxygen, 1.12; but .07 is to 1.12 as 1:16, and 1 part of hydrogen unites with 8 parts of oxygen (1 with $\frac{16}{2}$) to form water. The specific gravity of chlorine is 2.45, and the relationship is :— .07 : 2.45 : : 1 : 35.45; but the combining weight of chlorine is 35.45, as that part by weight of chlorine unites with one part of hydrogen. If we use hydrogen as unity* the relationship is seen more readily thus:

H = 1. Then the
combining weight of oxygen is 8.(or $\frac{16}{2}$) its specific gravity 16.
" " " chlorine is 35.45. " " 35.45.
" " " nitrogen is 4.66 (or $\frac{14}{3}$) " " 14.

The most reasonable supposition is that if equal volumes of gases bear a similar relationship by weight to each other as do the individual particles of which they are composed, then the numbers of particles in the gases themselves must bear a simple ratio to each other, as 1:2, 1:3 or 1:1, indeed most probably they have equal numbers of particles, for by such a theory we can explain the simple relationship between the combining volumes of gases, and this was the conclusion Gay Lussac arrived at in the course of his investigations. Thus, as equal volumes of hydrogen and chlorine unite to form hydrochloric acid and the ratio between the weights of equal volumes of the gases is the same as that between the individual particles, what could be simpler than to suppose that the volumes contained equal numbers of these particles? Dalton, however, soon pointed out a defect in this reasoning. Let us suppose we have a volume of hydrogen containing 1000 atoms, then an equal volume of chlorine will also contain 1000 atoms, the two unite, thus forming 1000 molecules of hydrochloric acid. The natural result would be,

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*The ratio between the weights of hydrogen and of an equal volume of air, is as .069: 1 or as 1: 14.4, hence any specific gravity with air as unity can be converted to hydrogen as unity by multiplying with 14.4.

$$\boxed{\begin{matrix}1000\\ \text{atoms}\\ \text{H}\end{matrix}} + \boxed{\begin{matrix}1000\\ \text{atoms}\\ \text{Cl}\end{matrix}} = \boxed{\begin{matrix}1000\\ \text{mols.}\\ \text{H Cl}\end{matrix}}$$

$$1\ \text{vol. H} + 1\ \text{vol. Cl} = 1\ \text{vol. H Cl}$$

for, as we have seen, the volume of the molecule exercises no influence on the volume of the gas. Nature, however, contradicts this reasoning, for we have seen that hydrogen and chlorine unite *without change of volume;* in other words, 1 volume of hydrogen + 1 volume chlorine = *2 volumes hydrochloric acid,** and it follows that if hydrogen and chlorine have equal numbers of atoms in equal volumes, then hydrochloric acid must have but one-half the number in the same volume for,

$$\boxed{\begin{matrix}1000\\ \text{H}\end{matrix}} + \boxed{\begin{matrix}1000\\ \text{Cl}\end{matrix}} = \boxed{\quad 100}\boxed{0\ \text{H Cl}}$$

$$1\ \text{vol. H} + 1\ \text{vol. Cl} = 2\ \text{vols.}\quad \text{H Cl}$$

so 1000 molecules of hydrochloric acid must occupy twice the volume occupied previously by 1000 atoms of hydrogen, and hence in one volume of hydrochloric acid there must be but 500 molecules. It was left for an italian physicist, Amadeo Avogadro, to explain this seeming discrepancy between theory and fact. Avogadro supposed the elementary gases to be composed of molecules instead of atoms. As a usual thing these molecules are composed of two atoms so that, accepting this hypothesis, we would arrive at the following result:

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* Let the pupil instead of using the expression "volume" substitute "liter" and the whole subject will appear more clear, thus,

1 liter hydrogen + 1 liter chlorine = 2 liters hydrochloric acid.

$$\boxed{\begin{matrix}1000\\ H_2\end{matrix}} + \boxed{\begin{matrix}1000\\ Cl_2\end{matrix}} = \boxed{\begin{array}{r|l}200 & 0\ H\,Cl\end{array}}$$

1 volume hydrogen + 1 volume chlorine = 2 vols. hydrochloric acid. A reaction of this kind would then consist simply of an interchange of the atoms composing the molecules so that, whereas we previously had molecules each of which was composed of atoms of the same kind, we now would have molecules each of which is composed of atoms which are of a different kind. This will be more apparent if we write the equation as follows:

$$\begin{matrix}H\text{—}H & & H \quad H\\ + & = & | \quad\; |\\ Cl\text{—}Cl & & Cl \quad Cl\end{matrix}$$

What is true then of the *volume* is true of the *individual molecule*, there being the same number of molecules in equal volumes; the terms volume and molecule can therefore be used interchangeably.

Simple as Arogadro's explanation was, it was not generally accepted by chemists, chiefly because he tried to apply it in cases where substances which never were in a gaseous state were concerned, so that it was not until many years later that it was universally adopted. It was then brought into prominence and is now one of our fundamental hypotheses, furnishing to us the best means of determining the molecular weights of chemical compounds and elements.

Let us suppose that we have a volume of hydrogen weighing two grams, then an equal volume of chlorine must weigh 70.9 grams, for the weights of equal volumes of elementary gases are to each other as their atomic weights and 1:35.45 : : 2:70.9.

$$1\text{ vol. H} + 1\text{ vol. Cl} = 2\text{ vols. H Cl}$$

$$\boxed{\begin{matrix}H\\ 2\text{ gr.}\end{matrix}} + \boxed{\begin{matrix}Cl\\ 70.9\text{gr}\end{matrix}} = \boxed{\begin{array}{r|l}H\,Cl & H\,Cl\\ 72. & 9\text{ grs.}\end{array}}$$

It follows that a volume of hydrochloric acid equal to that of the hydrogen taken must weigh $\frac{72.9}{2}$ grams or 36.45 grams, and therefore if the molecule of hydrogen is two, then the molecule of hydrochloric acid is 36.45; so that if hydrogen be two, the specific gravity of hydrochloric acid is equal to its molecular weight, and we will soon see that this rule can be made general as follows:

If hydrogen be placed at two, then the molecular weights and specific gravities of gases are the same number.*

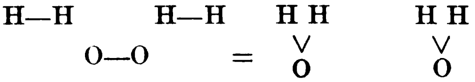
Hydrogen and oxygen unite to form water in the proportion of two volumes of hydrogen to one of oxygen, and if the water so formed is measured in the form of vapor we will find that two volumes of water are produced, thus:

$$\boxed{\begin{matrix}\text{H}\\ \text{1 vol.}\end{matrix}} + \boxed{\begin{matrix}\text{H}\\ \text{1 vol.}\end{matrix}} + \boxed{\begin{matrix}\text{O}\\ \text{1 vol.}\end{matrix}} = \boxed{\text{H}_2\,\text{O} \;\big|\; \text{2 vols.}}$$

If, according to Avogadro's hypothesis, oxygen has two atoms to the molecule, the reaction which takes place will be as follows:

$$\boxed{\begin{matrix}1000\\ \text{H}_2\end{matrix}} + \boxed{\begin{matrix}1000\\ \text{H}_2\end{matrix}} + \boxed{\begin{matrix}1000\\ \text{O}_2\end{matrix}} = \boxed{\begin{matrix}1000\\ \text{H}_2\,\text{O}\end{matrix}} + \boxed{\begin{matrix}1000\\ \text{H}_2\,\text{O}\end{matrix}}$$

or, as molecule and volume can be used interchangeably,



1 Mol. H + 1 Mol. H + 1 Mol. O = 2 Mols. Water.

Now, if each volume of hydrogen weigh two grams, then the same volume of oxygen will weigh thirty-two grams and consequently:

$$\boxed{\begin{matrix}\text{2 gr.}\\ \text{H}\end{matrix}} + \boxed{\begin{matrix}\text{2 grs.}\\ \text{H}\end{matrix}} + \boxed{\begin{matrix}\text{32 grs.}\\ \text{O}\end{matrix}} = \boxed{\begin{matrix}\text{18 grs.}\\ \text{H}_2\text{O}\end{matrix}} + \boxed{\begin{matrix}\text{18grs,}\\ \text{H}_2\text{O}\end{matrix}}$$

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* In dealing with the specific gravity of gases it is not necessary to deal with exact numbers. Thus, using the oxygen standard for atomic weights, hydrogen is 1.007, but for all practical purposes the decimal can be neglected.

Therefore in the case of water also, if hydrogen be two, the molecular weight and the specific gravity are identical, and similar methods of reasoning, backed by experiment, have shown us that in all cases the specific gravity of gases and their molecular weights have the same numerical value. The value of the discoveries just cited as an assistance in determining the atomic weights of elements is apparent. By a determination of the specific gravity of a gas we ascertain the relative weight of a molecule of that gas, as for instance in the case of water, the molecular weight cannot be more or less than eighteen, and in this eighteen parts by weight of water quantitative analysis shows us that we have sixteen parts by weight of oxygen and two of hydrogen. The atomic weight of oxygen therefore cannot be *more* than sixteen. The maximum number is consequently fixed by experiment. That it is not some fraction of sixteen we cannot state so definitely, yet all evidence points against this assumption. In the first place *two volumes* of hydrogen unite with *one* of oxygen to form water, the presumption therefore is that water has the formula H_2O and hence sixteen would be the atomic weight of oxygen, and in the second, *we never have encountered any compound of oxygen which can be obtained in a gaseous state, and whose molecular weight we therefore know, which contains less than sixteen parts by weight of that element.* The magnitudes at present in use for our atomic weights are the results of reasoning exactly similar to that given in the case of oxygen, assisted in many cases by deductions drawn from analogy between elements and by other less important methods of determining molecular weights, and we will subsequently see that the atomic weights at present in use are the only ones by means of which the elements, when arranged in the order of their atomic weights, naturally fall into series and families which show the greatest resemblance to one another. This existence of elements as molecules is used to explain the chemical activity of elements in the nascent state. (See page 50.)

Chemical equations expressing the changes which take place when simple or compound substances are brought in contact indicate the initial bodies and the final result *by formulae based upon our atomic weights,* taking no account of the changes of energy; they as a rule, represent only the *main course of a reaction* while other minor reactions are often going on in a mixture of two or more substances. Many equations are true only for certain conditions of temperature, concentration, etc. A chemical equation is simply an algebraic expression which can be constructed quite independently of chemical facts, and when so constructed is entirely useless if not pernicious in its tendency. We must always bear in mind that chemical facts and experiments are infinitely more valuable than chemical equations, the latter being only useful as a short method of expressing those changes which we know to take place.

In uniting to form hydrochloric acid, hydrogen and chlorine give 220 K. In dissolving in water an additional 70 K is evolved, so that the solution of hydrochloric acid in water possesses much less chemical energy than does the gas. We would therefore expect hydrochloric acid gas to enter into a number of reactions where the solution would be inert. If hydrochloric acid gas and oxygen are passed through a heated tube (see page 58) the following reaction takes place:

$$2\,HCl + O = H_2O + 2\,Cl,$$

while if chlorine water is allowed to stand in the sunlight:

$$2\,Cl + H_2O = 2\,HCl + O.$$

This contrast is explained by the difference in energy between gaseous hydrochloric acid and the solution for:

$$\begin{array}{rcl} H + Cl & = & HCl \text{ gives } 220\,K, \\ 2\,H + 2\,Cl & = & 2\,HCl \quad \text{''} \quad 440\,K, \\ 2\,H + O & = & H_2O \quad \text{''} \quad 680\,K, \end{array}$$

hence the heat of formation of water (the measure of the chemical energy of H and O) is greater than that of two molecules of hydrochloric acid gas and therefore the reaction $2\,HCl + O = H_2O + 2\,Cl$ would be accompanied by an evolution of heat. On the other hand,

$$\begin{array}{rcl} H + Cl & = & HCl \text{ dissolved in } H_2O \text{ gives } 390\,K, \\ 2\,H + 2\,Cl & = & 2\,HCl \quad \text{''} \quad \text{''} \quad \text{''} \quad \text{''} \quad 780\,K, \end{array}$$

and hence the heat of formation of dissolved hydrochloric acid is greater than that of water. As a result the reaction

$$2\,Cl + H_2O = 2\,HCl + O$$

in the presence of water is accompanied by an evolution of heat. Of course the more concentrated a solution of hydrochloric acid is the nearer will it approach the condition of the gas, and hence the greater will be its reactiveness. Similar studies with other bodies show us that the differences in energy between dissolved substances and those undissolved is often very marked, and in considering whether certain chemical reactions will take place we should take this difference into account.

The compound of hydrogen and chlorine is called an acid because it has certain distinctive properties possessed by every substance entitled to be classed as such.

An acid is a compound containing hydrogen united to a negative element or group of elements, which hydrogen can be replaced by a metal to form a salt.

No definition of an acid is entirely satisfactory, as we have a number of substances which contain hydrogen replaceable by a metal, as for instance water in the reaction $HOH + K = KOH + H$, yet we scarcely would call water an acid, nor KOH a salt, although, essentially there is no difference between this reaction and the following: $Zn + 2\,H\,Cl = Zn\,Cl_2 + 2\,H$, in one case it is the negative group of elements OH in the other the negative element Cl which is united to hydrogen, and the reaction takes place because K or Zn have a greater chemical energy when brought in contact with Cl or OH respectively than has hydrogen, they being more metallic in their nature than is hydrogen and hence presenting a greater contrast to the not-metal. If we call hydrochloric acid an acid and water not one, it is simply because expediency shows us that it is well to classify those hydrogen compounds, the hydrogen of which is easily replaced by a large number of elements to form salts, under the head of acids, an indication of the propriety of the name being that the substance designated as "acid" has the power of turning a blue vegetable, dye blue litmus, of a red color, yet it is evident that this latter distinction is purely arbitrary and unimportant as regards the true chemical nature of acids. Many substances which are not acids will turn blue litmus a red color, while on the other hand some substances decidedly acid* have no effect whatever upon litmus.

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* Organic substances acting as acids.

In forming chlorides we can have recourse to four methods, three of which illustrate general characteristics of acids; they are:

1st. By direct union of the elements, as

$$\begin{aligned} Na + Cl &= Na\,Cl. \\ Zn + 2\,Cl &= Zn\,Cl_2 \\ P + 3\,Cl &= P\,Cl_3 \\ C + 4\,Cl &= C\,Cl_4 \end{aligned}$$

This method leads to the formation of chlorides of the not-metals as well as those of the metals, the process being analogous to that of combustion in oxygen.

2d. By the action of hydrochloric acid on a *metal* when the chloride and hydrogen are produced, as:

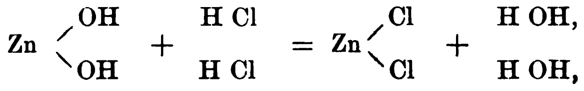
$$\begin{aligned} Zn + 2\,H\,Cl &= Zn\,Cl_2 + 2\,H, \\ Fe + 2\,H\,Cl &= Fe\,Cl_2 + 2\,H, \\ Mg + 2\,H\,Cl &= Mg\,Cl_2 + 2\,H. \end{aligned}$$

This reaction takes place with metals only.

3rd. By the action of hydrogen chloride on the oxides of metals when the chloride and water is produced, as:

$$\begin{aligned} Zn\,O + 2\,H\,Cl &= Zn\,Cl_2 + H_2\,O, \\ Ca\,O + 2\,H\,Cl &= Ca\,Cl_2 + H_2\,O, \\ Mg\,O + 2\,H\,Cl &= Mg\,Cl_2 + H_2\,O. \end{aligned}$$

4th. By the action of hydrogen chloride on the hydroxides of the metals, as:



$$Zn\begin{cases} OH \\ OH \end{cases} + \begin{matrix} H\,Cl \\ H\,Cl \end{matrix} = Zn\begin{cases} Cl \\ Cl \end{cases} + \begin{matrix} H\,OH, \\ H\,OH, \end{matrix}$$

$$\begin{aligned} Ca\,(OH)_2 + 2\,H\,Cl &= Ca\,Cl_2 + 2\,H_2\,O, \\ Mg\,(OH)_2 + 2\,H\,Cl &= Mg\,Cl_2 + 2\,H_2\,O. \end{aligned}$$

When an oxide or hydroxide reacts in the above manner it is the oxide or hydroxide of a metal, and is designated as a base; while the chemical process of forming a salt by addition of an acid to a base or base to an acid is called neutralization, (the acid or base are neutralized). This term "base" is one dictated by expediency, and when we speak of a substance as basic in character we mean it can form an oxide or a hydroxide which will neutralize acids.

The reactions under 3 and 4 are general to all acids and bases, if we designate any metal by M, any acid by HX, then the general rule will be that:

$M_2O + 2\,HX = 2\,MX + H_2O$, $MOH + HX = MX + H_2O$,
$MO + 2\,HX = MX_2 + H_2O$, $M(OH)_2 + 2\,HX = MX_2 + 2\,H_2O$,
$M_2O_3 + 6\,HX = 2\,MX_3 + 3\,H_2O$, $M(OH)_3 + 3\,HX = MX_3 + 3\,H_2O$.

Thus:

$K_2O + 2\,HNO_3 = 2\,KNO_3 + H_2O$, $KOH + HNO_3 = KNO_3 + H_2O$,
$ZnO + 2\,HBr = ZnBr_2 + H_2O$, $Zn(OH)_2 + 2\,HNO_3 = Zn(NO_3)_2 + 2\,H_2O$,
$Al_2O_3 + 6\,HNO_3 = 2\,Al(NO_3)_3 + 3\,H_2O$, $Al(OH)_3 + 3\,HNo_3 = Al(NO_3)_3 + 3\,H_2O$.

The metals differ among each other in their power of replacing hydrogen in acids to form salts, some replace one atom, some two, some three; but whatever the acid, this number always is the same and can be ascertained from the formula of the chloride of the metal (as KCl, $ZnCl_2$, $AlCl_3$), the metal will replace as many hydrogen atoms in any acid as there are chlorine atoms in the formula weight of its chloride, and the hydroxide will contain as many hydroxyle groups (OH) as there are chlorine atoms in the chloride.*

The reactions under 2 take place between a number of metals and acids, but the applications are much less general than 3 and 4, and often indeed, where the acid contains oxygen, no hydrogen is evolved, but some other substance is produced from the acid by the action of the hydrogen in the nascent state.

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* See pages 29 and 30.

CHAPTER X.

BROMINE AND HYDROBROMIC ACID.

Symbol Br, atomic weight 79.95, specific gravity of fluid 3.187, specific gravity of gas, below 900°, air = 1, is 5.52, H = 2 is 159.3. Symbol H Br, specific gravity, air = 1 is 2.79, H = 2 is 80.7, 1 *c.c. at* 0° *and* .76 *m. pressure weighs* .0036 *grams.*

In many respects bromine resembles chlorine, indeed such modifications in chemical characteristics as it represents are due simply to its larger atomic weight. It has the same tendency to unite with metals to form salts and hence is not free in nature but always combined as bromides, its compounds generally accompanying those of chlorine, yet always in lesser quantity, bromine being one of the rarer elements. The bromides of sodium and magnesium are found in the great majority of salt springs, especially in those of Saratoga Springs, in the Saginaw Valley and in the southeastern portion of Ohio where the bromide of potassium also occurs. In Europe the brines from the salt works of Kreuznach and Strassfurth are especially rich in bromides. Marine fauna and flora also frequently contain bromides. The brines of the various salt works are evaporated, thus crystallizing the sodium chloride for the manufacture of table salt, there remaining a not crystallizable brine (mother liquor) which is especially rich in bromides. In this mother liquor, Ballard discovered bromine in 1826, calling it bromine from βρῶμος, a stench.

Bromine is prepared from its compounds in a manner entirely analogous to the method used in isolating chlorine. A bromide is mixed with manganese dioxide and sulphuric acid (see pages 58, 59) when the following reaction takes place:[33]

$$2\ Na\ Br + 2\ H_2\ SO_4 + Mn\ O_2 = Mn\ SO_4 + Na_2\ SO_4 + 2\ Br.$$

Hydrobromic acid and manganese dioxide would yield bromine just as hydrochloric acid and manganese dioxide would give us chlorine;

$$4\,HBr + MnO_2 = MnBr_2 + 2\,Br + 2\,H_2O$$
$$4\,HCl + MnO_2 = MnCl_2 + 2\,Cl + 2\,H_2O$$

but owing to the difficulty of preparing hydrobromic acid the latter substance is an expensive article, so that from reasons of economy this latter method is not available.

Bromine is a dark brown liquid, almost black when any considerable thickness is observed, it melts at —7.3° and boils at 63.05°, a point considerably below the boiling point of water. The specific gravity of the liquid at 0° is 3.18. When the liquid is allowed to stand in the air it evaporates rapidly even at ordinary temperatures, yielding reddish brown vapors very irritating to the mucous membrane of the eyes, nose and throat, and possessing an odor much resembling that of chlorine. The specific gravity of the vapor, air being 1 at 800° is 5.42, giving 159.3 as its density $H = 2$. This shows that at this temperature the molecule of bromine is constructed of two atoms like that of chlorine, for the atomic weight is 80, so that 160 would be the molecular weight of Br_2. Above 1200° the specific gravity of the vapor decreases until it becomes 3.7 showing that at high temperatures some of the Br_2 molecules have changed to individual atoms.

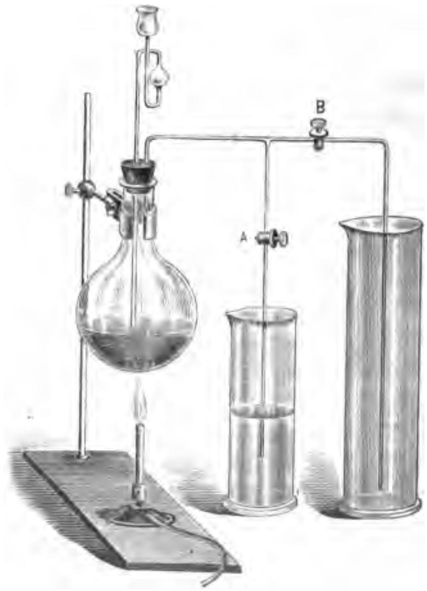


FIGURE 15.

Bromine is soluble in water, the solution having a brownish color and properties similar to those of chlorine water; one part of bromine at 15° being soluble in 33 parts of water. If this solution is cooled to the freezing point of water, crystals of a compound of bromine with water of crystallization ($2\ Br + 10\ H_2O$) separate. (See Page 60).

The solution of bromine in water is an oxidizing agent and hence bleaches just as chlorine water did; this property is due to the same cause, the liberation of oxygen.

$$2\,Br + H_2O = 2\,H\,Br + O.$$

The formation of oxygen becomes apparent if a tube containing bromine water is inverted over a water trough and exposed to the sunlight; oxygen separates as it did with chlorine water, although perhaps, not with such great rapidity.*

The compounds of bromine resemble those of chlorine in every particular and the bromides and chlorides of the same metal are isomorphous.†

Bromine does not unite with hydrogen as readily as does chlorine, its higher atomic weight rendering its chemical character less negative and hence its tendency to unite with metals less pronounced; as a consequence a mixture of bromine and hydrogen can be allowed to stand in the sunlight for any length of time without the formation of hydrobromic acid; the union is only to be brought about by more energetic means, such as the electric spark or the passing of a mixture of hydrogen and bromine over platinized asbestos.

The heat of formation of hydrobromic acid gas is only 121 K. while that of gaseous hydrochloric acid is 220 K, so that we would expect it to be decomposed by the application of less energy. The consequences of the resulting instability are unpleasantly apparent in the difficulties encountered in the preparation of hydrobromic acid.

In preparing hydrochloric acid we had but to treat sodium chloride with sulphuric acid, as follows:

$$2\,Na\,Cl + H_2\,SO_4 = Na_2\,SO_4 + 2\,H\,Cl, \text{ and}$$

a similar reaction takes place when a bromide is substituted for a chloride;

$$2\,Na\,Br + H_2SO_4 = Na_2\,SO_4 + 2\,H\,Br;$$

---

* Owing to the greater ease with which bromine is handled it is more frequently in use as a laboratory oxidizing agent than is chlorine.

† See page (42) and foot note.

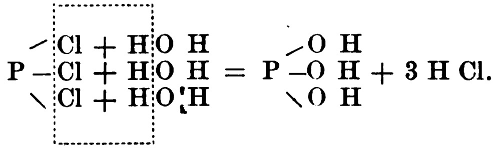
but hydrobromic acid, being so much less stable than hydrochloric, breaks down into hydrogen and bromine, after which the nascent hydrogen attacks the sulphuric acid, reducing the latter to form sulphur dioxide and water:

1. $2\,H\,Br = 2\,H + 2\,Br$
2. $H_2SO_4 + 2\,H = 2\,H_2O + SO_2$;

and as a consequence the hydrobromic acid formed is contaminated with sulphur dioxide.

In order to prepare hydrobromic acid for laboratory use advantage is taken of the instability of the halogen compounds of the not-metals.

When $P\,Cl_3$, phosphorus trichloride, was added to water the following change took place:



Phosphorus trichloride + water = Phosphorus hydroxide (Phosphorous acid) + hydrochloric acid.

$$P\,Cl_3 + 3\,H_2O = P\,(OH)_3 + 3\,H\,Cl.$$

The same with phosphorus tribromide:

$$P\,Br_3 + 3\,H_2O = P\,(OH)_3 + 3\,H\,Br.$$ 34

In performing this operation it is not necessary to employ the finished tribromide of phosphorus as a mixture of phosphorus, bromine and water will answer the same purpose.

Hydrobromic acid is a colorless gas, with an acid odor resembling that of hydrochloric acid; it fumes strongly in the air, owing to the absorption of moisture; it is extremely soluble in water, one part of that substance absorbing as much as 82 per cent. of hydrobromic acid and as a consequence the gas cannot be collected over water. If a quantity is desired this must either be separated by collecting over mercury or by displacement of air in some vessel, for as the specific gravity of hydrobromic acid is 2.79 it can be poured downward.

As has already been stated, hydrobromic acid is much less stable than is hydrochloric acid and therefore on adding chlorine to the former, bromine is separated and hydrochloric acid formed.

$$HBr + Cl = HCl + Br.$$

In its chemical behavior hydrobromic acid is like hydrochloric acid. When brought in contact with bases it neutralizes them to form salts.

$$\begin{array}{llll} NaOH & + \; HBr & = Na\,Br & + HOH \\ KOH & + \; HBr & = H\,Br & + HOH \\ CaO & + \; 2\,HBr & = Ca\,Br_2 & + H_2O. \end{array}$$

The methods of formation of the bromides are analogous to those of the chlorides. They are,

1. Direct union of the element in question with bromine, this applying to metal or not-metal.
2. The addition of a metal to hydrobromic acid, when the bromide and hydrogen are formed.
3. The action of hydrobromic acid on the oxides or hydroxides of the metals, when the bromides and water are produced.

Hydrobromic acid is formed of one volume of hydrogen and one volume of bromine vapor united to form 2 volumes of hydrobromic acid, the same considerations advanced under chlorine show that the bromine molecules, provided the temperature be not too high, consist of two atoms to the molecule. (See pages 68, 69, 70.)

CHAPTER XI.

IODINE AND HYDROIODIC ACID.

Symbol I, atomic weight 126.85, specific weight 4.948, specific weight of vapor, air = 1, is 8.76 (below 600°), H = 2 is 253.56. Symbol HI, *specific weight, air = 1, is 4.41, H = 2 is 127.2,* 1 c.c. *of the gas at* 0° *and* .76 *m. weighs* .0057 *grams.*

This last member of the halogene family is not found as such in nature, in that way it resembles fluorine, chlorine and bromine; its compounds, although they occur in company with those of chlorine and bromine in almost all their deposits, are not found by any means in such large quantities. The element occurs in sea water as the iodide of sodium or magnesium, although in such small quantities that its presence cannot be proved unless some special means are taken to separate it. Sea plants such as the algae, as well as representatives of the animal kingdom, sea sponges, crabs, oysters, etc., can assimilate and concentrate those traces of iodides so that, on drying and burning, iodine can easily be proved to be present in the ashes. The iodides occur in salt springs, in deposits of rock salt, in a number of mineral springs as at Kreuznach and Reichenhall, in river water and also in some water plants growing in flowing fresh water.

The element was discovered in 1811 by Courtois, a saltpeter manufacturer in Paris, who found its compounds in the mother-liquors left after extracting the ashes of sea plants and crystallizing the less soluble portions. The name iodine is from ἰωδης, violet. The weed which is washed up on the islands on the western coast of Scotland or of Ireland or on the coast of Normandy by the spring storms, or that which grows upon the rocks, is dried and burned, the fused mass remaining as the ash is brought into the market under the Scotch name of kelp or Normanic, varec. The amount of iodine contained in this as iodides is very small and is extracted from the last remaining mother-liquors obtained by crystallizing the aqueous extract of kelp. The method of preparation of iodine is identical with that of chlorine or bromine;[85] the iodide is treated with sulphuric acid and manganese dioxide:

$$Mn\,O_2 + 2\,KI + 2\,H_2\,SO_4 = Mn\,SO_4 + K_2\,SO_4 + 2\,H_2\,O + 2\,I.$$

In order to purify the iodine it is sublimed, the iodine being heated in retorts and collected as crystals in cold chambers.

The element is an almost black, greyish solid, with a luster closely resembling that of the metals, when pure and fused it is entirely black, in thin plates it is translucent with a brownish-red color. Its specific weight is 4.94, it melts at 113°–115° and boils at 200°, when heated in a vacuum it does not melt but vaporizes without fusion. The vapor of iodone has a beautiful violet color* and a specific gravity, air being 1, of 8.84 below 600°, giving a density, $H = 2$ of 255.21, showing that below this temperature iodine has a molecule consisting of two atoms, I_2, but if the heat is gradually increased the specific gravity of the vapor diminishes, so that at 1500° it is only, air $= 1$, 5.67, or $H = 2$, 163.69, indicating that the vapor of iodine at bright red heat consists of a mixture of the individual atoms, and the molecules I_2, dissociation beginning above 600°. Iodine is but very litle soluble in water, about 7000 parts of water dissolving one part of iodine, but water containing salts in solution has a greater solvent action; some solutions such as those of potassium iodide and of hydroiodic acid have the power of dissolving large quantities of iodine, the element is also extremely soluble in substances such as alcohol, ether, carbon bisulphide or chloroform.

Chemically, iodine resembles chlorine or bromine, it unites with sulphur, phosphorus and other not-metals with which the other halogenes form compounds, in combination with the metals it forms iodides, and if hydrogen mixed with iodine vapors is passed over spongy platinum heated, some hydroiodic acid is formed, although hydroiodic acid is an endothermic compound and therefore possesses more energy than the individual elements of which it is composed.

When the preparation of hydrobromic acid was mentioned we saw that the method available for hydrochloric acid was not feasible owing to the relative instability of hydrobromic acid, the latter breaking down into hydrogen and bromine, while the hydrogen reduced the sulphuric acid to sulphurous acid. As a consequence we were compelled to use the reaction depending on the decomposition of the bromide of phosphorus by water. We could not, therefore, expect to obtain hydroiodic acid by the action of sulphuric acid on sodium iodide, for hydroiodic acid decomposes even more readily than hydrobromic, the reaction taking place so energetically that sulphuretted hydrogen ($H_2 S$) is produced. If we write the equations representing the action of hydrobromic and hydroiodic acid upon sulphuric acid, this relative instability at once becomes apparent,

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* Observe the same by throwing some iodine on a hot stove or into a hot porcelain crucible.

$$H_2 SO_4 + 2 H Br = 2 H_2 O + SO_2 + 2 Br,$$
$$H_2 SO_4 + 8 HI = H_2 S + 4 H_2 O + 8 I,$$

for in the latter case the reduction is much more energetic and far-reaching.*

In the preparation of hydroiodic acid therefore, we are compelled to resort to a round-about method similar to that employed in the production of hydrobromic acid; the reaction used depending on the instability of the iodide of phosphorus in the presence of water.

$$PI_3 + 3 H_2 O = P (OH)_3 + 3 HI.$$

Of course a mixture of iodine, water, and red phosphorous answers the purpose.[36] Hydroiodic acid can be collected in empty jars by displacement of air, or it can be collected over mercury; its extreme solubility in water renders the filling of vessels with the gas impossible where water is present.

Hydroiodic acid is a colorless gas with the acid odor of hydrochloric or hydrobromic acid, it fumes in the air, owing to absorption of moisture. Its specific weight is 4.37, air being 1, H being 2, it is 126; the molecular weight of HI is 127.85, the discrepancy

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*This reaction illustrates quite well the influence exerted by the *mass* of the chemical reagents used. If a large excess of sulphuric acid and but little hydroiodic are present, a considerable quantity of sulphur dioxide (SO_2) is produced, while generally more or less sulphur is deposited. These changes are represented by the equations:

$$H_2 SO_4 + 6 HI = 4 H_2 O + S + 6 I,$$
$$H_2 SO_4 + 2 HI = 2 H_2 O + SO_2 + 2 I.$$

Under ordinary conditions, in a test tube, all of these changes take place at the same time so that the equation given in the text only represents one of the various changes going on, a variation of temperature or mass of the reagents can alter the proportions of $H_2 S$, sulphur or SO_2 produced.

between the observed specific gravity and the molecular weight being due, undoubtedly, to the difficulties encountered in obtaining pure hydroiodic acid. Hydroiodic acid is quite easily condensed to a liquid; at —17.8°c. its vapor tension is but two atmospheres, it solidifies at —51°c. On heating, hydroiodic acid is easily decomposed, the change into hydrogen and iodine beginning at 180° and being complete at 700°. Chlorine decomposes hydroiodic acid with explosive violence, forming hydrochloric acid and iodine.

Hydroiodic acid is composed of equal volumes of hydrogen and iodine; two volumes of hydroiodic acid yield one of hydrogen and one of iodine, provided the temperature be kept sufficiently high to vaporize the iodine formed. The gas is extremely soluble in water, the solution when saturated at 12° contains 57.7 per cent. of hydroiodic acid; it must be kept well stoppered and in the dark; for, when exposed to the air a separation of iodine takes place, owing to the formation of water, as follows:

$$2\,HI + O = H_2O + 2\,I.$$

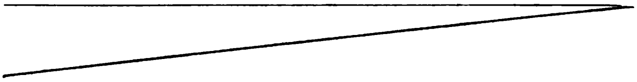
Hydroiodic acid has a strongly acid reaction, turning blue litmus solution red and in all respects resembling hydrochloric and hydrobromic acids, the methods of formation of the iodides being exactly like those of bromides and chlorides. The heat of formation of gaseous hydroiodic acid from hydrogen and solid iodine is —61 K, from gaseous iodine and hydrogen almost nil, the heat of solution is 192 K, so that the heat of formation of hydroiodic acid in water is 131 K. The gaseous acid is therefore an endothermic compound, possessing a tendency to decompose into its constituent parts; the solution possesses much less chemical energy and hence greater stability. In the following table a comparison of the properties of the halogenes has been undertaken, their differences with increasing atomic weight thus becoming more apparent.

THE HALOGENES.

	F.	Cl.	Br.	I.
	Colorless gas.	Greenish yellow gas.	Dark brown liquid.	Black solid.
Density of liquid..	——	1.33	3.18	4.97

Density of vapor.	air = 1 ——	2.45	5.54	8.7
	H = 2 ——	70.73	159.9	254.
Molecule of gaseous element........	——	Cl_2	Br_2	I_2

The density of iodine vapor at 447° is 8.7, at 1500° the density is 4.76 which yields 137.4 as the density, H = 2. Dissociation is therefore almost complete at this temperature, so that the molecule and atom of I nearly correspond.

	HF.	H Cl.	H Br.	HI.
Stability.				
Heat of formation......	——	H, Cl=220 K.	H, Br=84 K.	H, I=—61 K.
Ditto, plus water......	——	393 K.	283 K.	131 K.

Chlorine replaces bromine when brought in contact with bromides and iodine when brought in contact with iodides.

Bromine replaces iodine in the iodides.

Fluorine liberates oxygen from water, even in the dark.

$$2\,F + H_2O = 2\,HF + O.$$

Chlorine liberates oxygen from water in the sunlight.

$$2\,Cl + H_2O = 2\,H\,Cl + O.$$

Bromine liberates oxygen from water in the sunlight more slowly than Cl.

Iodine does not decompose water.

CHAPTER XIII.

THE OXYGEN FAMILY.

Three elements—sulphur, selenium and tellurium—show a relationship toward oxygen similar to that displayed by chlorine, bromine and iodine toward fluorine. With increasing atomic weights we have similar changes in the physical properties of the elements, illustrating the decreasing not-metallic characteristics of the family; oxygen being a colorless gas, sulphur a yellow solid, selenium a dark red solid in one of its allotropic forms, while tellurium is an element having entirely the appearance of a metal. All of the elements of this family form hydrogen compounds which, with the exception of water, are colorless gases at ordinary temperatures. In this they resemble the halogenes, for in that family the hydrogen compound of the element with the smallest atomic weight, fluorine, is liquid at ordinary temperatures; the compounds with hydrogen, of the members of the oxygen family, however, have one atom of the element united to two of hydrogen, these atoms therefore display a power of retaining hydrogen atoms in close proximity which is twice as great as that possessed by the halogenes; the formulæ are H_2O, H_2S, H_2Se, H_2Te. The stability and heat of formation of these compounds diminishes with increasing atomic weight, accompanying the decreasing not-metallic properties of the elements in a manner exactly parallel to the similar changes in the halogene family, so that hydrogen selenide decomposes at about the same temperature as hydroiodic acid (150°) while hydrogen telluride is not known in a pure state and decomposes even at ordinary temperatures, if in contact with the air. The hydrogen compounds of this family are by no means as acid in their properties as those of the halogenes*—indeed, water does not redden litmus, while hydrogen sulphide, selenide or telluride do not turn blue litmus into a pronounced red. The hydrogen compounds of the three latter elements are much less soluble in water than those of the halogenes.

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*The acid properties of the hydrogen compounds of the not-metals diminish with an increase in the number of hydrogen atoms in the molecule.

In comparing HF, H_2O, and H_3N we see that hydrofluoric acid, as its name implies, is a pronounced acid; water only acts like an acid when brought in contact with the most pronounced metals such as sodium or potassium, (sometimes it can act as a base), while ammonia, H_3N, is basic in its character. This gradation of properties is possibly due to the increasing predominence of the positive element, for it is obvious that three hydrogen atoms will have a much greater effect in determining the nature of a compound than one; hence H_3N as an entire compound is positive. As the negative element in the hydrogen compounds increases in atomic weight its larger mass may cause its character to become more prominent; hence H_3 Sb is not basic, antimony having next to the highest atomic weight in the family of which nitrogen is a member.

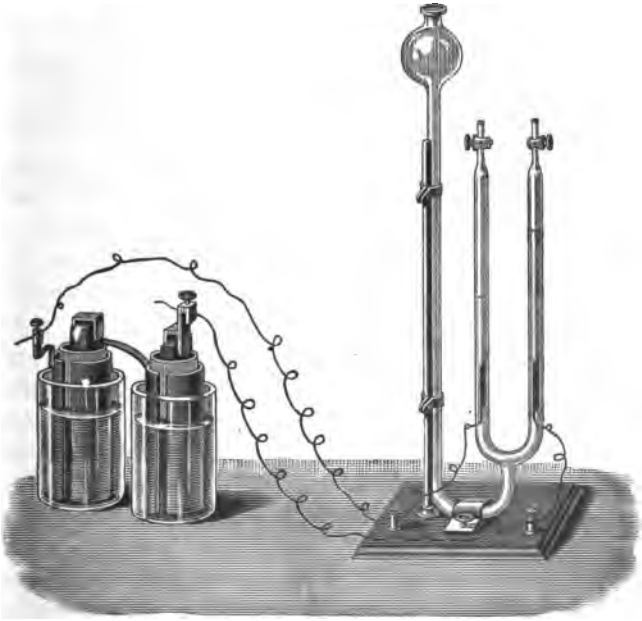

FIGURE 16.

The study of the hydrogen compounds of the oxygen family is less completely finished than is that of the corresponding compounds of the halogenes, for hydrogen selenide and hydrogen telluride have rarely been prepared in a pure state.

The elements of this family, with the possible exception of tellurium, exist in two allotropic forms. They form compounds with oxygen which are anhydrides of acids, the study of which will be deferred. The compounds of sulphur, selenium and tellurium with the metals have formulæ which correspond to those of the oxides, thus:

Na_2O	Na_2S.	Na_2Se	Na_2Te
Sodium oxide;	Sodium sulphide;	Sodium selenide;	Sodium telluride.
FeO,	FeS.	$FeSe$	$FeTe$
Ferrous oxide;	Ferrous sulphide;	Ferrous selenide;	Ferrous telluride,

furnish a few examples.

Oxygen has already been discussed, so that the study of this family will be continued with sulphur.

CHAPTER XIV.

SULPHUR.

Atomic weight 32.06, symbol S, specific gravity of solid 2.045, specific gravity of vapor (above 1000°) air = 1, is 2.2, hydrogen = 2, is 63.3.

Sulphur is found, often in company with gypsum or limestone, in volcanic regions such as those of southern Italy and of Sicily. In Europe the largest quantities come from the provinces of Girgenti and Catania in Sicily; the crater of the volcano Purace in South America, with a surface of about 1200 square yards, is covered with a layer of sulphur more than a yard in thickness; while in our own country considerable quantities of sulphur are found in California. The element occurs, combined, chiefly in the sulphides, the most important of which are the sulphide of iron $Fe S_2$, iron pyrites; $Pb S$, galenite; $Zn S$, zinc blende and $Cu Fe S_2$, chalcopyrite. Sulphur also occurs united with oxygen and a metal in the sulphates of calcium, $Ca SO_4$, barium, $Ba SO_4$, Magnesium, $Mg SO_4$, etc.; the most important of these is gypsum, $Ca SO_4 + 2 H_2 O$. Many organic compounds such as mustard oils contain sulphur.

Sulphur has been known from very ancient times, having been used as a medicine by the Greeks and Romans. The alchemists considered it an essential portion of all combustible substances, while during the period in which the phlogiston theory was believed in, it was looked upon as a compound of sulphuric acid with phlogiston. After our present chemical theories were initiated by Lavoisier's studies on oxidation, sulphur was classed as an element.

Of course, as sulphur is found uncombined, any method for preparing the element from its compounds is of no essential value in the laboratory. Sulphur might be furnished, just as was chlorine, bromine or iodine, by treating its hydrogen compound with some oxidizing agent, for instance by mixing a sulphide with manganese dioxide and adding sulphuric acid, which would be a

In its chemical behavior, in many respects, sulphur closely resembles oxygen; where the former metal forms oxides, the latter forms sulphides with similar formulæ:

OXIDES.	SULPHIDES.
$Na_2 O$,	$Na_2 S$,
$K_2 O$,	$K_2 O$,
$Fe O$,	$Fe S$,
Fe_3O_4,	$Fe_3 S_4$,
$P_2 O_3$,	$P_2 S_3$,
$P_2 O_5$.	$P_2 S_5$,

and these sulphides can be prepared by direct union of the elements, just as were the oxides. Furthermore there are sulphydrates, which correspond to the hydroxides in formula:

$Na OH$,	$Na SH$,
KOH,	KSH.

The sulphides and sulphydrates of the metals resemble the bases; with acids they form salts and sulphuretted hydrogen, while the latter forms salts and water, thus:

$$Na_2 S + 2 H Cl = 2 Na Cl + H_2 S.$$
$$Na_2 O + 2 H Cl = 2 Na Cl + H_2 S.$$
$$Na SH + H Cl = Na Cl + H_2 O.$$
$$Na OH + H Cl = Na Cl + H_2 O.^*$$

The sulphides of the not-metals sometimes resemble the anhydrides of acids: forming salts with the sulphides of the metals, in such salts the oxygen has been replaced by sulphur, for example:

$$CS_2 + Na_2 S = Na_2 CS_3$$

Carbon disulphide + Sodium sulphide = Sodium sulphocarbonate.

$$CO_2 + Na_2 O = Na_2 CO_3$$

Carbon dioxide + Sodium oxide = Sodium carbonate.

In these reactions carbon bisulphide and sodium sulphide bear the same relationship to each other as sodium oxide and carbon dioxide do. Sulphur also resembles chlorine, bromine or iodine, in some ways, for the sulphides can be prepared as were the compounds of those elements: for example when phosphorus and sulphur are thick that it can no longer be poured; at about 340° it once more becomes fluid, but remains of a dark color. Its boiling point lies at 440° centigrade which temperature it changes to a dark brown vapor.[38] The specific gravity of this vapor, air being 1, at about 470° is 7.9 but upon increasing the temperature this gradually diminishes until 1000°is reached when the density is 2.3. At the latter temperature the molecule of sulphur resembles that of oxygen, hydrogen and chlorine, for it consists of two atoms.[*]

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* Many sulphides are not attacked by acids under ordinary circumstances and the same may be said of a number of oxides. Many such are found as minerals. Wherever the sulphides are dissolved by acids, they act like bases.

Sulphur exists in two allotropic forms; one soluble in carbon bisulphide, the other insoluble. The soluble can be partially changed into the insoluble one by melting or by exposure to the sunlight. Both forms occur in the sulphur of commerce, flowers of sulphur being especially rich in the insoluble variety.

Sulphur can exist in four crystalline forms, only two of which are easily obtainable and of importance.[†] When deposited from its solutions in carbon bisulphide, it crystallizes in octahedra belonging to the rhombic system (Fig. 25), but if sulphur is melted and allowed to cool slowly it forms long prismatic needles, (monoclinic system) as in Fig. 26.[39] The latter form changes into the former on standing; the needles becoming opaque and while apparently retaining their crystalline form, finally consist only of an aggregation of rhombic crystals. During this process heat is evolved, and therefore the rhombic stable variety of sulphur possesses less energy than the other.

Sulphur, when heated to just below its boiling point and subsequently rapidly cooled by pouring into cold water, forms a plastic mass somewhat resembling india rubber; this gradually becomes hard and changes to yellow sulphur. The soft sulphur is dark in color, probably by reason of impurities; it contains both soluble and insoluble sulphur; sulphur crystals are sometimes entirely soluble.[‡]

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[*] It is generally considered that the molecule of sulphur consists of six atoms at temperatures just above the boiling point; but the recent investigations of Biltz seem to show that sulphur has no definite vapor density below 1000°. Molecules of greater complexity than S_2 may exist; these gradually, with increasing temperature, decompose into simpler ones. The specific gravity of 7.9 indicates (hydrogen being 2) a specific gravity of 227.5 which corresponds to a molecule S_7.

[†] A substance which exists in two crystalline forms is said to be dimorphous, one existing in three, trimorphous, one existing in many, polymorphous.

[‡] Plastic sulphur is often formed when sulphur is separated from its compounds by chemical means, as for instance in the oxidation of many of the sulphides of metals with nitric acid.

In its chemical behavior, in many respects, sulphur closely resembles oxygen; where the former metal forms oxides, the latter forms sulphides with similar formulæ:

OXIDES.	SULPHIDES.
$Na_2 O$,	$Na_2 S$,
$K_2 O$,	$K_2 O$,
$Fe O$,	$Fe S$,
$Fe_3 O_4$,	$Fe_3 S_4$,
$P_2 O_3$,	$P_2 S_3$,
$P_2 O_5$,	$P_2 S_5$,

and these sulphides can be prepared by direct union of the elements, just as were the oxides. Furthermore there are sulphydrates, which correspond to the hydroxides in formula:

$Na OH$,	$Na SH$,
KOH,	KSH.

The sulphides and sulphydrates of the metals resemble the bases; with acids they form salts and sulphuretted hydrogen, while the latter forms salts and water, thus:

$$\begin{aligned} Na_2 S &+ 2\,H\,Cl = 2\,Na\,Cl + H_2 S, \\ Na_2 O &+ 2\,H\,Cl = 2\,Na\,Cl + H_2 S, \\ Na\,SH &+ H\,Cl = Na\,Cl + H_2 O, \\ Na\,OH &+ H\,Cl = Na\,Cl + H_2 O.^{*} \end{aligned}$$

The sulphides of the not-metals sometimes resemble the anhydrides of acids; forming salts with the sulphides of the metals, in such salts the oxygen has been replaced by sulphur, for example:

$$CS_2 \quad + \quad Na_2 S \quad = \quad Na_2 CS_3$$

Carbon disulphide + Sodium sulphide = Sodium sulphocarbonate.

$$CO_2 \quad + \quad Na_2 O \quad = \quad Na_2 CO_3$$

Carbon dioxide + Sodium oxide = Sodium carbonate.

In these reactions carbon bisulphide and sodium sulphide bear the same relationship to each other as sodium oxide and carbon dioxide do. Sulphur also resembles chlorine, bromine or iodine, in some ways, for the sulphides can be prepared as were the compounds of those elements; for example when phosphorus and sulphur are

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[*] Many sulphides are not attacked by acids under ordinary circumstances and the same may be said of a number of oxides. Many such are found as minerals. Whenever the sulphides are dissolved by acids, they act like bases.

heated together, a sulphide of phosphorus is formed, just as was the case when phosphorus was heated in chlorine, for then a chloride was produced. Iron-filings heated with sulphur will form the sulphide of iron, just as the same substance heated with chlorine will form the chloride. Besides the above resemblances, many of the sulphides of the not-metals are decomposed by water, forming an acid and hydrogen sulphide, just as the chlorides of the same elements are decomposed forming an acid and hydrogen chloride, for example:

1. $P_2 S_3 + 6 H_2 O = 2 H_3 PO_3 + 3 H_2 S$,
2. $P_2 S_5 + 8 H_2 O = 2 H_3 PO_4 + 5 H_2 S$.

1. $P Cl_3 + 3 H_2 O = H_3 PO_3 + 3 H Cl$,
2. $P Cl_5 + 4 H_2 O = H_3 PO_4 + 5 H Cl$.

The acid formed in reactions 1 is phosporous acid, in reactions 2 is phosphoric acid. The tendency to form oxygen compounds of the not-metals in most cases is greater than that to form similar compounds of the other elements.

CHAPTER XV.

SULPHURETTED HYDROGEN.

Symbol H_2S, *specific gravity, air* $= 1$, *is* 1.17, $H = 2$, *is* 33.7, 1 c.c. *of gas weighs .00152 grams.*

Sulphuretted hydrogen occurs mixed with other gases and vapors in some volcanic exhalations, and also sometimes in coal and other mines. As it is one of the products of the decay of various animal and vegetable substances, it is necessarily frequently present in the atmosphere and in water. Many sea plants exposed to the sun's rays give off sulphuretted hydrogen and when organic substances such as bituminous coal, which contain sulphur, are heated without access to the air,* sulphuretted hydrogen is found in the gases given off. Many mineral waters contain large quantities of sulphuretted hydrogen; these come from sulphur springs; the gas can be detected by its peculiar odor, which resembles that of rotten eggs.

Sulphuretted hydrogen has certainly been known since the sixteenth or seventeenth century; later it was more accurately studied by Scheele, who considered it as composed of heat, sulphur and phlogiston. After Lavoisier's time its true nature was explained.

Sulphuretted hydrogen can be prepared with some difficulty by passing hydrogen through molten sulphur. When we recall that hydrogen unites with explosive violence with either oxygen or chlorine; the diminished energy with which hydrogen and sulphur or hydrogen and bromine unite, becomes apparent. Sulphuretted hydrogen is prepared for laboratory use by the action of some acid on a sulphide; for instance:

$$\begin{aligned} \mathrm{Fe\ S} + \mathrm{H_2\,SO_4} &= \mathrm{Fe\ SO_4} + \mathrm{H_2\,S}, \\ \mathrm{Fe\ S} + 2\,\mathrm{H\,Cl} &= \mathrm{Fe\ Cl_2} + \mathrm{H_2\,S}, \\ \mathrm{Zn\ S} + \mathrm{H_2\,SO_4} &= \mathrm{Zn\ SO_4} + \mathrm{H_2\,S}, \end{aligned}$$

---

* Called dry distillation.

the oxide or the chloride would act in exactly the same way:

$$\begin{aligned}
&Fe\,O + H_2\,SO_4 = Fe\,SO_4 + H_2\,O,\\
&Fe\,Cl_2 + H_2\,SO_4 = Fe\,SO_4 + 2\,H\,Cl,\\
&Zn\,O + H_2\,SO_4 = Zn\,SO_4 + H_2\,O,\\
&Zn\,Cl_2 + H_2\,SO_4 = Zn\,SO_4 + 2\,H\,Cl,
\end{aligned}$$

so that there is no essential difference between the action of a base and that of these other compounds in the presence of sulphuric acid; indeed were sulphides and chlorides and not oxides the most frequent chemical compounds, or were hydrochloric acid and sulphuretted hydrogen and not water produced in many reactions, the term base would never have been used to designate the oxide.[40]

Sulphuretted hydrogen is a colorless gas with an intensely disagreeable odor; it liquifies at a temperature of 11° with a pressure of fifteen atmospheres. It boils at ordinary pressures at—61.8° and becomes solid at—85°; it is tolerably soluble in water, for at ordinary temperatures one volume of water dissolves two volumes of the gas. The solution slightly reddens litmus, but the red color disappears on exposure to the atmosphere. Sulphuretted hydrogen is very poisonous; when inhaled in small quantities it causes headache, loss of appetite, dizziness, and inflammation of the eyelids, while persons who have been poisoned by sulphuretted hydrogen often have fainting spells at intervals during some weeks. Death may be caused by $\frac{1}{800}$ of a volume of sulphuretted hydrogen in the atmosphere.

When a stream of the gas is lighted, it burns to form water and sulphur dioxide, a mixture of two volumes of sulphuretted hydrogen and three of oxygen is highly explosive; where an insufficient supply of oxygen is present during the combustion of the gas, it deposits sulphur. Both chlorine and bromine decompose sulphuretted hydrogen in a manner similar to oxygen, forming hydrobromic or hydrochloric acid:

$$\begin{aligned}
&H_2\,S + O = H_2\,O + S,\\
&H_2\,S + 2\,Cl = 2\,H\,Cl + S,\\
&H_2\,S + 2\,Br = 2\,H\,Br + S.
\end{aligned}$$

In each of these three cases the reason for the reaction is found in the excess of the heat of formation of water, hydrochloric acid and hydrobromic acid over that of sulphuretted hydrogen. Iodine does not decompose sulphuretted hydrogen when no water is present, because in the production of hydroiodic acid heat is absorbed, but if the reaction takes place in contact with water, the heat of solution of hydroiodic acid is sufficient to cause the following change to take place:

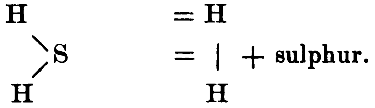
$$H_2S + 2I = 2HI + S.$$

The foregoing will be understood by placing the heats of formation of these various compounds side by side:

$H_2O = 684$ K,
$2HCl = 440$ K,
$2HBr = 186$ K,
$2HI = -122$ K, while
$2HI$ dissolved in water $= 262$ K.

Now, the heat of formation of sulphuretted hydrogen is but 27 K, the heat of solution in water is 46 K, therefore the heat of formation of hydrogen sulphide in water is 73 K; a number is much smaller than any of those given above.

Hydrogen sulphide is readily decomposed into its elements, just as were hydrobromic and hydroiodic acids, so that the former cannot be prepared in the presence of concentrated sulphuric acid any more than the two latter could, and it follows that sulphuretted hydrogen cannot be dried by being passed through sulphuric acid. A hot wire placed in the gas will dissociate it;[41] no change in the volume takes place, because the volume of the sulphur separated is minimal when compared with the volume of the gas as a whole, and therefore, the hydrogen occupies the same space as that previously taken by sulphuretted hydrogen:



$$1 \text{ volume } H_2S = 1 \text{ volume } H_2.$$

This fact proves, provided Avogadro's hypothesis is correct, that in a molecule of sulphuretted hydrogen there are contained two atoms of hydrogen.

We assume that there is but one atom of sulphur because of the analogy between water and sulphuretted hydrogen and also because, while H_2S contains two parts by weight of hydrogen and thirty-two of sulphur, *in no compound, the molecular weight of which has been determined and which contains sulphur, is that element found with a proportional weight smaller than thirty-two.*

Hydrogen sulphide resembles the acids, because in cases where it reacts with the oxide or hydroxide of a metal, the corresponding sulphide or sulphydrate is formed:

$$\begin{aligned}
\mathrm{Ca\,O} + \mathrm{H_2\,S} &= \mathrm{Ca\,S} + \mathrm{H_2\,O},\\
\mathrm{Ca\,O} + \mathrm{2\,H\,Cl} &= \mathrm{Ca\,Cl_2} + \mathrm{H_2\,O},\\
\mathrm{Na\,OH} + \mathrm{H\,SH} &= \mathrm{Na\,SH} + \mathrm{H\,OH},\\
\mathrm{Na\,OH} + \mathrm{H\,Cl} &= \mathrm{Na\,Cl} + \mathrm{H\,OH},
\end{aligned}$$

Sulphuretted hydrogen contains two atoms of hydrogen which can be replaced by metals so that we must distinguish two series of compounds, in the first of which one of these atoms is substituted as in $\mathrm{Na\,SH}$, in the second two as in, $\mathrm{Ca\,S}$. We shall subsequently see the same rule will hold good with all acids containing two replaceable hydrogen atoms.

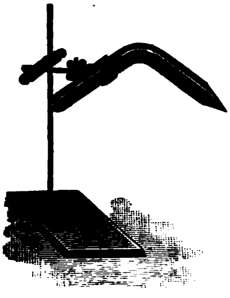


FIGURE 17.

The sulphides of a large number of metals are insoluble in dilute acids, so that where sulphuretted hydrogen is passed into a solution containing a salt of one or more of these these metals, the corresponding sulphide is precipitated:

$$\begin{aligned}
\mathrm{Cu\,SO_4} + \mathrm{H_2\,S} &= \mathrm{Cu\,S} + \mathrm{H_2\,SO_4},\\
\mathrm{Pb\,[NO_3]_2} + \mathrm{H_2\,S} &= \mathrm{Pb\,S} + \mathrm{2\,H\,NO_3},\\
\mathrm{Cd\,Cl_2} + \mathrm{H_2\,S} &= \mathrm{Cd\,S} + \mathrm{2\,H\,Cl}.
\end{aligned}$$

The sulphides of some metals are soluble in dilute acids, but insoluble in water or in alkalies; these will not be precipitated unless provision is made to neutralize the acid formed. This can be accomplished either by passing sulphuretted hydrogen into a solution rendered alkaline by the addition of ammonium or sodium hydroxide solutions, or better by adding a soluble sulphide.

$$\mathrm{Na_2\,S} + \mathrm{Zn\,SO_4} = \mathrm{Zn\,S} + \mathrm{Na_2\,SO_4}.$$

Lastly, the sulphides of a third class of metals are soluble both in acid or alkaline water, these will of course not be precipitated by sulphuretted hydrogen. The action of sulphuretted hydrogen on the salts of the metals is a ready means of detecting the presence of the metals in a solution, and many of the processes of qualitative analysis are founded upon these reactions, so that a further discussion belongs to that branch of applied chemistry.

In addition to hydrogen sulphide there exists another compound of hydrogen and sulphur called hydrogen persulphide. This latter has the formulæ $H_2 S_2$;* a yellow, oily fluid with a penetrating odor and corrosive action. It resembles its prototype, hydrogen dioxide, $H_2 O_2$, in the fact that it is stable in the presence of dilute acids, and in the ease with which it decomposes into sulphur and sulphuretted hydrogen, just as that did into water and oxygen.

---

* This may be the formulæ of the compound, although this is not definitely settled. There may exist more than one persulphide of hydrogen or the reason of varying amounts of sulphur in the persulphide may be due to sulphur dissolved by that substance.

CHAPTER XVI.

SELENIUM AND HYDROGEN SELENIDE.

Symbol Se, atomic weight 79.1, specific gravity, 4.5, specific gravity of vapor, above 1400°, air = 1, is 5.7; H = 2, is 164 (calculated for Se_2 158.2). Symbol H_2 Se, specific gravity air = 1, is 2.8; H = 2 is 80.6.

Selenium occurs in selenides just as sulphur was found in sulphides; much more sparingly however. Free selenium is only very rarely found in some volcanic regions. The chief selenides are those of lead (Pb Se) and of iron (Fe Se), while the selenide of silver (Ag_2 Se) also occurs. Lately, considerable quantities of selenium combined with bismuth have been found in some parts of South America.

Selenium was discovered by Berzelius in 1817 in the lead chambers used in the manufacture of sulphuric acid. He at first confused the element with tellurium, but subsequently proved it to be a hitherto unknown element, which he called selenium from σελήνη, moon, because the name of the other element was derived from *tellus* earth.

The occurrence of selenium in the sulphuric acid chambers and in the flues of furnaces in which sulphides are roasted is due to the presence of selenium in the ores (such as iron pyrites, copper pyrites or zinc blende). The selenium is burned to selenium dioxide and mechanically carried into the flues and chambers when the sulphides are roasted. Selenium dioxide is easily reduced to selenium by means of reducing agents such as sulphur dioxide,* so that the dust of the chambers contains the greater portion selenium in the form of the element. The isolation of selenium is quite a complicated process, and a description of the methods must be left to a larger work.

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* Reducing agents are such substances as are capable of removing oxygen or the equivalent of oxygen from chemical compounds, or they are such substances as can add hydrogen to elements or compounds.

Selenium exists in two allotropic forms, one soluble, the other insoluble in carbon bisulphide, in that way resembling sulphur. When selenium is separated from its compounds by chemical means it is a crimson powder when moist, dark red and soluble in carbon bisulphide when dry; by heating this above 80° it becomes iron grey in color. The elements melts at 217° and boils at 665°, and then, when cooled suddenly, is insoluble in carbon bisulphide. The selenium of commerce is formed by casting melted selenium into sticks. It is almost metallic in its appearance and black in color. Selenium can exist in more than one crystalline form, in that way resembling sulphur.

Chemically, the properties of selenium are closely akin to those of sulphur. It burns in the air, forming selenium dioxide just as the latter formed sulphur dioxide. The selenides and selenium compounds in general have formulæ exactly like those of the corresponding sulphur compounds. The element is of little importance excepting in a comparative study of the elements.

Hydrogen selenide is the complete analogon of hydrogen sulphide. It can be prepared with difficulty by the direct union of the elements, being obtained by passing hydrogen over selenium heated to its boiling point; however, unless great care is taken to regulate the temperature, the heat will decompose the hydrogen selenide so formed. The gas can also be prepared by adding an acid to the selenide of iron:

$$\mathrm{Fe\,Se} + 2\,\mathrm{H\,Cl} = \mathrm{Fe\,Cl_2} + \mathrm{H_2\,Se},$$

in a manner analogous to the preparation of hydrogen sulphide.

Hydrogen selenide is a colorless gas, with a most penetrating odor somewhat resembling that of sulphuretted hydrogen; it is extremely poisonous.* The gas, upon being heated, begins to decompose at a temperature of 150°, but is only completely dissociated at a considerably higher temperature. It burns even more readily than did sulphuretted hydrogen and of course is decomposed by chlorine or bromine, or by iodine in the presence of water. It is more soluble in water than is sulphuretted hydrogen, and has the same action upon soluble salts of the metals as the latter.

---

* Care must be taken in working with the gas, for its odor clings to the clothes for many days.

CHAPTER XVII.

TELLURIUM AND HYDROGEN TELLURIDE.

Symbol Te, atomic weight 125, specific gravity 6.25, specific gravity of vapor, air = 1, is 9, H = 2, is 259, (above 1400°). Symbol H_2 Te.

Tellurium resembles both selenium and sulphur, it occurs as telluride of silver, gold, lead, and also as tellurium. It was discovered in 1782 and identified as an element in 1798. It is very rare and of comparatively little importance. Its preparation from its ores is a complicated process. It is a silver white, metallic appearing element, which melts at about 500° and boils at a high temperature, forming an orange colored vapor. The element is with difficulty obtained free from selenium. Like sulphur and selenium it exists both as amorphous and crystalline tellurium.

Hydrogen telluride was discovered by Davy in 1810. It is best prepared by adding hydrochloric acid to zinc or magnesium telluride:

$$\mathrm{Zn\ Te} + 2\ \mathrm{H\ Cl} = \mathrm{H_2\ Te} + \mathrm{Zn\ Cl_2}.$$

It is a colorless gas which entirely resembles the hydrogen compounds of sulphur and selenium. It burns readily, with a blue flame and is gradually decomposed into hydrogen and tellurium even at ordinary temperatures. It is instantly changed on exposure to the air:

$$\mathrm{H_2\ Te} + \mathrm{O} = \mathrm{H_2\ O} + \mathrm{Te}.^*$$

The tellurides are with difficulty obtained pure and are prepared like the sulphides and selenides.

A comparative table of the elements of this family will serve to render the relationship between them and the resemblance of this family to the halogenes more apparent:

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* Compare this with the action of hydroiodic acid when exposed to the air.

	Atomic weight.	Specific gravity of solid.	Melting point.	Boiling point.		Not-metallic properties.
O	16.	——	——	—181°	Gas.	∨
S	32.06	2.04	114°	440°	Yellow solid,	
Se	79.1	4.5	217°	665°	Dark red powder, black when fused.	
Te	125.	6.25	500°	above 1000°	Silver white, metallic appearance.	

	Specific gravity of vapor. air = 1.	Specific gravity of vapor. H = 2.	Molecule.	
O	1.1	31.76	O_2	* The molecular weights $Se_2 = 158$, $Te_2 = 250$ are somewhat less than the specific gravities found, but near enough to show that the molecule exists as two atoms. † The specific gravities of sulphur and selenium vapors are not constant below 1000°, they gradually become larger as the boiling points are approached. The molecules S_2 and Se_2 seem to form larger aggregations as the elements approach the temperature of liquification, no definite formulæ seem assignable to these molecules.
S	2.2	64.3†	S_2	
Se	5.7	164.*†	Se_2	
Te	9.	259.*	Te_2	

	Heat of formation.	Stability.		Heat of formation.	Stability.	
H_2O	684 K	∨	2 HF	——	∨	All of the hydrogen compounds are colorless gases above 100° centigrade.
H_2S	27 K		2 H Cl	480 K		
H_2Se	—111 K		2 H Br	168 K		
H_2Te	——		2 HI	—122 K		

On comparing the atomic weights of the elements of the oxygen family with those of the halogenes we see that the former are, throughout, somewhat smaller for corresponding elements, *the difference however is but slight.*

O	16	F	19
S	32	Cl	35.5
Se	79	Br	80
Te	125	I	127

CHAPTER XVIII.

VALENCE AND THE OXYGEN COMPOUNDS OF THE NOT-METALS.

The elements, the properties of which we have studied, formed compounds with hydrogen, all of which, with two exceptions—hydrogen dioxide and the corresponding sulphur compound—could be obtained as vapors, the specific gravities and hence the molecular weights of which could therefore readily be ascertained. By this means we arrived at the conclusion that chlorine, bromine or iodine could unite with but one atom of hydrogen, while oxygen and the remaining members of that family could unite with two. These ele-elements therefore differed among themselves in their power of retaining hydrogen atoms. In addition to the foregoing there are other elements, the hydrogen compounds of which are composed of three atoms of hydrogen to one of the negative element; these elements are nitrogen, phosphorus, arsenic and antimony. If we designate any one of these elements by Y then the formula of the hydrogen compounds would be YH_3. Only two other elements, carbon and silicon, form gaseous hydrogen compounds; the general formula of these is ZH_4. All hydrogen compounds can therefore be classed under four heads:

$$VH,\ XH_2,\ YH_3,\ ZH_4.^*$$

From the outset we have considered chemical compounds as formed by the conjunction of the atoms of elements; the atoms themselves are hypothetical,† but using this hypothesis as a basis, a chemical theory productive of the greatest results has been developed.

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* We can immagine all apparent variations from these types as formed by the substitution of one or more of these hydrogen atoms by some other element, or groups of elements. Thus, we have considered sodium hydroxide as water, in which one atom of hydrogen has been replaced by sodium; Na-O-H, H-O-H. hydrogen dioxide as water, in which one atom of hydrogen has been replaced by hydroxyle H-O—O-H, H—O-H. and so on.

† Sir William Tnompson considers them to be rings formed by vortical motion of the ether, a visible example of such motion would be a smoke ring blown by a locomotive.

"Every finite quantity of matter occupies a position in space which is definable with regard to other material particles, the question as to the relative position (or motion) of atoms in the molecule is scientifically justified, and must be put sooner or later"[*] by persons holding the atomic theory. This problem has been put by chemists ever since the time of Berzelius and the great advance in organic chemistry, which has been reflected in inorganic chemistry, is the result of its successful solution. In the hydrogen compounds of the not-metallic elements we are cognizant of the number of atoms in the molecule, *because we have been able to determine the quantitative composition of these compounds and also the molecular weight.*

As the mass of the atom of the not-metal in hydrogen compounds is so much greater than that of the hydrogen, and as in the formation of new chemical compounds from those of hydrogen it is always the hydrogen which is replaced by some other element, provided the resulting compound remains identical or similar in character, it is more than probable that the hydrogen atoms are joined to the not-metal. Whether the *position* of these is fixed, or whether they are free to rotate around the not-metal we cannot decide, but recent investigation all tends toward the former theory. In the compounds VH, XH_2, YH_3 and ZH_4 the numerical capacity possessed by the not-metal of uniting with one, two, three and four atoms of hydrogen is termed the *valence* of the element, and we can conveniently express this valence by roman numerals placed over the symbol of the not-metal, $\overset{I}{V}$, $\overset{II}{X}$, $\overset{III}{Y}$, $\overset{IV}{Z}$, or by lines drawn from them, as $V-$, $-X-$, $-\overset{|}{Y}-$ or $-\underset{|}{\overset{|}{Z}}-$. The element which can unite with one atom of hydrogen is termed *univalent*, that which can unite with two, *bivalent*, with three, *trivalent* and with four *quadrivalent*; hydrogen is always univalent. All elements whose valence is more than one can be called polyvalent. When a univalent element has united with another element or radical[†] its capacity for further union has ceased; a bivalent element however, when united with an element or radical by one valence has not lost its capacity of further union with other elements or radicals, it is *unsaturated*, for instance, $H—X—$ is in this condition and can act as a univalent radical. Similarly $H—\overset{\overset{H}{|}}{Y}—$ is also unsaturated and univalent, $H—\overset{|}{Y}—$ unsaturated and bivalent, $H—\underset{|}{\overset{\overset{H}{|}}{Z}}—H$, $H—\underset{|}{\overset{\overset{H}{|}}{Z}}—$ and $H—\underset{|}{\overset{|}{Z}}—$, unsaturated and respectively uni, bi and trivalent.

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[*] W. Ostwald, Outlines of General Chemistry. Walker's translation.

[†] A group of elements which can, as a whole, replace an element in a chemical compound is called a radical.

Only the not-metals, however, form hydrogen compounds obtainable as gases, so that with other elements, if we desire a similar means of determining valence, we must seek for gasifiable compounds with some univalent element other than hydrogen. Many of the metals and of the not-metals are capable of forming such compounds with chlorine, the molecular weights of these can therefore be determined.

The halogenes form compounds with formulæ analogous to those of hydrogen, and such compounds can obviously be used to determine the valence of the elements; for if the number of hydrogen atoms with which an element is united in a molecule indicates the valence of that element, so must the number of chlorine atoms in a similar molecule. We can therefore construct a table containing a series of chlorine compounds, just as we did with the hydrogen compounds, and further investigation shows us that all of these compounds can be brought under six heads; using M as a general term to denote an atom of an element with the capacity of uniting with chlorine, we have:

$M\,Cl$, $M\,Cl_2$, $M\,Cl_3$, $M\,Cl_4$, $M\,Cl_5$, $M\,Cl_6$, and using roman numerals to designate the valence—

$$\overset{I}{M}, \overset{II}{M}, \overset{III}{M}, \overset{IV}{M}, \overset{V}{M}, \overset{VI}{M}.$$

In many cases where a hydrogen compound of a given element exists, we can also study the chlorine compound, so that a determination of the valence of the elements by means of the chlorine compounds offers the advantage of being applicable in a greater number of cases. Sometimes, as is the case with some metals, the bromide or iodide is obtainable as a gas, while the chloride is not; then the former compounds answer just as well as a means of determining the valence. In our considerations we have, so far, always been able to appeal to experiment to answer any questions which may arise, in those which follow we will have to indulge more or less in speculation.

Can elements, polyvalent toward hydrogen, unite with each other, and, if so, what is their valence? The answer to the first part of the question has already been given, we have become aware of compounds such as CO_2, SO_2, CS_2 all of which are formed by the union of polyvalent elements, and in these cases, as in the vast majority of those which fall within the scope of this book, one atom of one of the elements in the molecule unites all the others; furthermore, compounds such as CO_2, SO_2 or CS_2 can have their molecular weights determined in the same way as those of hydrogen, so that the same reasoning will apply with the former as with the latter. We could therefore suppose such compounds formed in the manner of water, H—O—H, O—C—O, O—S—O, S—C—S, in which case carbon or sulphur would be bivalent, as is oxygen in water, and indeed any theory other than this as regards the valence of the elements in such compounds of bivalent elements goes beyond the realm of facts absolutely proved by experiment; yet the majority of chemists have thought themselves justified in holding other views, and a few of the reasons for their opinions may not be out of place here. Oxygen unites with two atoms of hydrogen to form water so that in this compound it is undoubtedly bivalent; furthermore, oxygen is capable of uniting with two atoms of any other univalent element, such as sodium or potassium, the oxides of which are Na_2O, K_2O, and the element can also unite two univalent radicals or groups of elements to form compounds (calling any radical q) of the formula q—O—q, so that an atom of this element can serve as a link between groups of element, a function which is necessarily impossible for univalent elements. When oxygen replaces hydrogen in the compounds of that element one atom of the former always takes the place of two of the latter, for instance the compound CH_4 in being oxidized forms in addition to water first, $C\genfrac{}{}{0pt}{}{H_2}{O}$ and then, $C\genfrac{}{}{0pt}{}{O}{O}$; CH_4 +

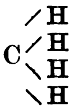
$2O = CH_2O + H_2O$; and $CH_2O + 2O = CO_2 + H_2O$. The valence of elements can also be given by the formulæ of the chlorides, and when a chloride is converted into an oxide, one atom of oxygen always replaces two of chlorine:

CHLORIDES.	OXIDES.
$2\,NaCl$	Na_2O
$2\,KCl$	K_2O
$CaCl_2$	CaO
$FeCl_2$	FeO
$2\,AlCl_3$	Al_2O_3
$2\,FeCl_3$	Fe_2O_3
CCl_4	CO_2
$2\,PCl_3$	P_2O_3.*

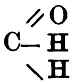
From these considerations it is supposed that oxygen remains bivalent wherever it enters into chemical combination. In assuming this to be the case we must consider an atom of oxygen as being united to other elements differently than is hydrogen, and applying what we learned in regard to univalent elements, where we saw that when one univalent element united to another its further power of union is exhausted, we can construct the following arbitrary rule:

One valence of any element in a chemical compound always calls for and neutralizes a corresponding valence in the other element or elements with which it is united.

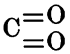
The two valences of a bivalent element, therefore, are supposed to neutralize two corresponding valences in any element or compound with which it is united. The following examples will serve to make this meaning more clear:



CH_4, quadrivalent carbon.



Two atoms of univalent hydrogen replaced by one of bivalent oxygen, carbon remaining quadrivalent.



Four atoms of univalent hydrogen replaced by two of bivalent oxygen, carbon remaining quadrivalent.

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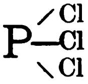
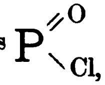
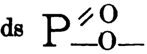
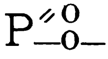
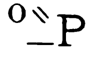
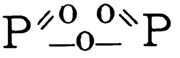
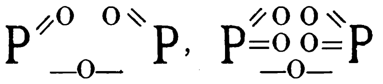
* All of the chlorides in this list have been obtained as gases, their molecular weights and formulæ are certain, the corresponding oxides have not, but *having once determined the atomic weights of the elements* the formulæ of such compounds follow from their composition by weight.

Where an atom of a polyvalent element has an odd number of valences it follows that these cannot be neutralized by those of an atom of a bivalent element without leaving one atom of the latter unsaturated:

 with oxygen yields  phosphorus remaining trivalent, and this yields  *with one oxygen atom unsaturated,* this unites with some other element or group of elements, so that;  +  becomes  phosphorus remaining trivalent and oxygen uniting the two univalent groups of atoms. By a similar application of the rule we can come to the conclusion that where five oxygen atoms unite with two of some other polyvalent element the latter is quinquivalent; where three unite with one it is hexavalent so that the following table of oxides can be constructed, using X to denote an atom of any element:

X_2O,	valence of X one;	denoted by	$\overset{I}{X}_2O$
$X\ O$,	" " X two;	"	" $\overset{II}{X}\ O$
X_2O_3,	" " X three;	"	" $\overset{III}{X}_2O_3$
$X\ O_2$,	" " X four;	"	" $\overset{IV}{X}\ O_2$
X_2O_5	" " X five;	"	" $\overset{V}{X}_2O_5$
$X\ O_3$	" " X six;	"	" $\overset{VI}{X}\ O_3$
X_2O_7	" " X seven;	"	" $\overset{VII}{X}_2O_7$
$X\ O_4$	" " X eight;	"	" $\overset{VIII}{X}\ O_4$

The formulæ of all oxides with a very few exceptions correspond to these general formulæ, and what has been said of oxygen applies to all other bivalent elements. In endeavoring therefore to ascertain the valence of an element forming an oxide, we must consider all of the oxygen atoms in the molecule to be retained by the atoms of the element just as was the case with the hydrogen and chlorine compounds, we must by analysis ascertain the gravimetric composition, so that we can learn the number of atoms united in the formula weight; where we can obtain the compound as a gas we must learn its specific gravity and by this means its molecular weight. For instance, there are two oxides of phosphorus, in one of which 62 parts by weight of phosphorus unite with 48 of oxygen, in the other 62 of phosphorus with 80 of oxygen. From the study of many compounds of oxygen and phosphorus we have concluded that the atomic weights of these two elements are 16 and 31 respectively, hence the composition by weight of the first of the two compounds leads us to a formula $P_2 O_3$, that of the second to a formula $P_2 O_5$. Now we can construct two formulæ by writing out the individual atoms, grouping them together so that connecting lines will express the valences, as follows:



$P_2 O_3$, $P_2 O_5$,

Such diagrams constructed of chemical symbols, expressing a theory regarding the manner in which atoms are grouped in a chemical compound, are called structural formulæ. These can be more or less complete in expressing the ideas of those using them to picture the position of the atoms in a molecule. The two given above are not intended to show more than that the oxygen atoms are all united to those of phosphorus by means of two valences apiece, and that the two phosphorus atoms are united to each other by means of the interposed oxygen atom; other formulæ however might be constructed illustrating a theory regarding the relative position of all of the atoms, as has been done with compounds of carbon in organic chemistry, where recent investigation has brought chemistry so far that the relative positions in space of atoms forming a molecule can be studied. It will only fall within the scope of this work to use structural formulæ such as those above.

A trivalent element can unite with bivalent elements, with other trivalent elements or with a quadivalent element, it can unite three univalent radicals and so on, its valence remaining three, one valence in uniting neutralizes another, as in the case of uni and bivalent elements; we also could develop similar theories with the other polyvalent elements.

Such are briefly the rules which, for the sake of uniformity, are used by the majority of chemists. In applying such methods chemists are apt to allow themselves to forget how far experiment has gone, and thus to confuse the theory and its application with the phenomena of nature. The terms "valence" or "bond," used to express the means of union between atoms thus becomes to them a material thing, the lines used on paper to express the manner of union of atoms become, in imagination, real linkings between existing atoms, so that at the present time the science of chemistry is in danger of being discredited by a too dogmatic conception of valence, and so one of her greatest achievments of recent times, the theory of valence, may ultimately prove a serious obstacle in the path of her development. In comparing two compounds such as H–O–H and O–C–O we cannot, without indulging in speculations, assert more than that in one case oxygen has the capacity of retaining two atoms of hydrogen in a molecule, and that in the other carbon presents the same relationship toward oxygen, the supposition that oxygen is retained in the molecule CO_2 by a force differing in its manifestations from the one retaining hydrogen in H_2O is purely

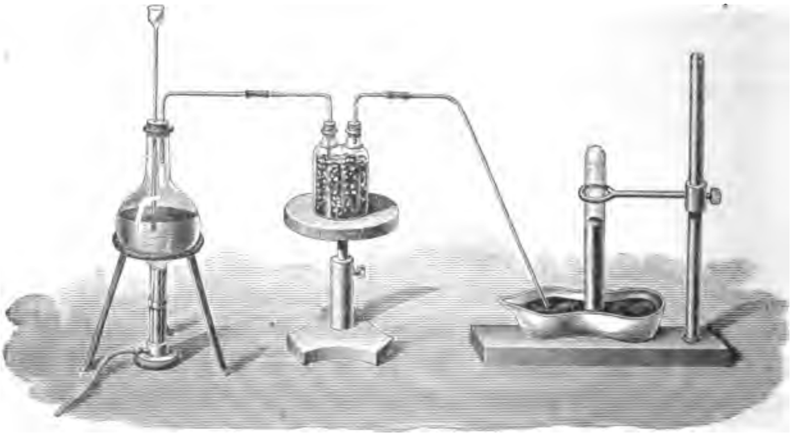


FIGURE 18.

gratuitous and based upon the action of oxygen and hydrogen in entirely different compounds. Where we have heretofore not ascertained the molecular weight of a compound, as is the case with P_2O_3 and P_2O_5, experiment can only show us the composition of such compounds by weight; of the structure and size of the real molecule and of the manner of union of the atoms in this molecule, wehave no knowledge, our rules of valence can only be applied to the formula weight therefore. If however we remember where the boundary between speculation and experiment lies we, will very much simplify the study of chemistry by the application of these rules. The valence of the atom of an element is, as much as any other property of that element, determined by the family in which that element belongs and hence by its atomic weight. The position of an element in the periodic system of the elements therefore offers one of the best means of determinng its valence.

An atom may under differing conditions vary the number of oxygen atoms with which it unites, thereby changing its valence; the not-metals are especially prone each to form a number of oxides. All of the not-metals with the exception of fluorine and bromine have oxides which are constructed according to certain types. The following is a table of those oxides which are most frequently recurring; as will be seen the same general formula often belongs to compounds in more than one family; X, in each family is used to represent a typical element:

Halogenes.	Oxygen family.	Nitrogen family.	Carbon family.
$\overset{\text{I}}{X}_2O$	$\overset{\text{IV}}{X}O_2$	$\overset{\text{I}}{X}_2O$*	$\overset{\text{IV}}{X}O_2$
$\overset{\text{III}}{X}_2O_3$	$\overset{\text{VI}}{X}O_3$	$\overset{\text{III}}{X}_2O_3$	
$\overset{\text{V}}{X}_2O_5$		$\overset{\text{V}}{X}_2O_5$	
$\overset{\text{VII}}{X}_2O_7$			
Highest valence seven.	Highest valence six.	Highest valence five.	Highest valence four.

* This oxide does not form an acid on addition of water but a corresponding acid is known, which breaks down into water and thisoxide.

When the oxide of a not-metal is the anhydride of an acid and is changed to the acid by the addition of water, the valence of the atoms of the element which characterizes that anhydride is not supposed to be changed; such a change can only be effected by either oxidation or reduction. One or two examples will make this apparent. Cl_2O * is a compound in which the two atoms of chlorine are united to one of oxygen; chlorine being univalent and the structural formula comparable with that of water:

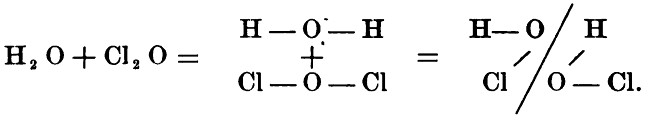
$H-O-H$	$Cl-O-Cl$
Water.	**Chlorine monoxide.**

When chlorine monoxide is added to water the following change takes place:

$$Cl_2O + H_2O = 2\,HOCl$$

Chlorine monoxide + Water = Hypochlorous acid.

The nature of this becomes more apparent if written as follows:



$$H_2O + Cl_2O = \begin{matrix} H-O-H \\ + \\ Cl-O-Cl \end{matrix} = \begin{matrix} H-O & / & H \\ / & / & / \\ Cl & / & O-Cl. \end{matrix}$$

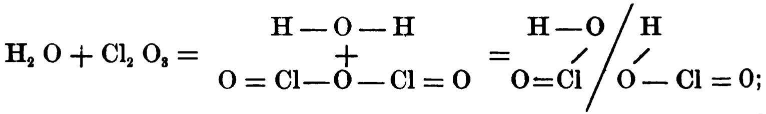
Whether we consider $H-O-Cl$ as water in which the atom of hydrogen is replaced by one of chlorine, or as chlorine monoxide in which one atom of chlorine is replaced by one of hydrogen is a matter of indifference,—*chlorine obviously remains univalent* in the acid, as it was in the anhydride. Now, in order to change Cl_2O to Cl_2O_3 *we must add oxygen,*

$$Cl-O-Cl + 2\,O = O=Cl-O-Cl=O.$$

The process of oxidation leaves the group of atoms $Cl-O-Cl$ intact. Such a group as this is entirely independent of any added valence assumed by chlorine. Now, when Cl_2O_3 reacts with water:

$$Cl_2O_3 + H_2O = 2\,HO_2Cl$$

Chlorine trioxide + Water = Chlorous acid, or



$$H_2O + Cl_2O_3 = \begin{matrix} H-O-H \\ + \\ O=Cl-O-Cl=O \end{matrix} = \begin{matrix} H-O & / & H \\ / & / & / \\ O=Cl & / & O-Cl=O; \end{matrix}$$

---

* X_2O under the head of halogenes in the above table.

† It is scarcely necessary to remind the pupil that the oxygen atom so added must be fixed by chlorine, the oxygen in $Cl-O-Cl$ being bivalent, is incapable of further union.

the valence of chlorine remains three, for the added oxygen atoms have not changed the nature of the reaction. What is true of Cl_2O and Cl_2O_3 must be true of X_2O or X_2O_3, and by similar structural formulæ we can show that when the reactions

$$X_2O_5 + H_2O = 2\,HO_3X, \text{ and } X_2O_7 + H_2O = 2\,HO_4X$$

take place, the valence of X remains unaltered, for the point of attack for the water is the oxygen uniting the two univalent atoms or groups of atoms. With the other class of anhydrides given in the table named *i. e.* those formed by not-metals having an even number of valences, the addition of water has no different result. As there is but one atom of the uniting element present in these oxides the entire molecule of water must add itself thereto, but a little consideration will show us that the change is identical with those we have discussed, for an oxygen atom present in the anhydride, with the addition of a molecule of water, forms two hydroxyle groups:

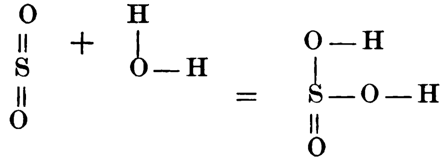
a. $SO_2 + H_2O = H_2SO_3$

Sulphur dioxide + Water = Sulphurous acid.

$SO_3 + H_2O = H_2SO_4$

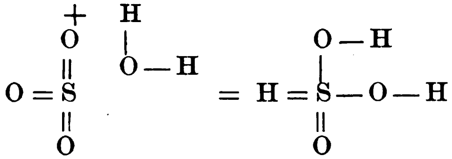
b. Sulphur trioxide + Water = Sulphuric acid.

a.



$$\begin{array}{c} O \\ \| \\ S \\ \| \\ O \end{array} + \begin{array}{l} H \\ | \\ O-H \end{array} = \begin{array}{l} O-H \\ | \\ S-O-H \\ \| \\ O \end{array}$$

b.



$$\begin{array}{r} + \\ O \\ \| \\ O=S \\ \| \\ O \end{array} \begin{array}{l} H \\ | \\ O-H \end{array} = \begin{array}{l} O-H \\ | \\ H=S-O-H \\ \| \\ O \end{array}$$

When SO_2 is changed to SO_3 by oxidation, the valence of sulphur is changed, but obviously the added oxygen atom plays no more part in the reaction upon addition of water than it did in the cases previously considered. The water which is taken up by anhydrides is therefore decomposed by them, it breaks down into H and -O-H, The hydrogen attaches itself to oxygen while the hydroxyle group unites with the atom which characterizes the anhydride. *Water,* therefore, does not enter into the composition of the acids, but *hydroxyle* groups do. In the following table are placed the general formulæ of the oxides previously considered and the corresponding acids; X, as heretofore, denoting the not-metal:

$$\overset{\mathrm{I}}{X}_2O + H_2O = 2\,HO\,\overset{\mathrm{I}}{X}$$

$$\overset{\mathrm{III}}{X}_2O_3 + H_2O = 2\,HO_2\,\overset{\mathrm{III}}{X}$$

$$\overset{\mathrm{V}}{X}_2O_5 + H_2O = 2\,HO_3\,\overset{\mathrm{V}}{X}$$

$$\overset{\mathrm{VII}}{X}_2O_7 + H_2O = 2\,HO_4\,\overset{\mathrm{VII}}{X}$$

$$\overset{\mathrm{IV}}{X}\,O_2 + H_2O = H_2O_3\,\overset{\mathrm{IV}}{X}$$

$$\overset{\mathrm{VI}}{X}O_3 + H_2O = H_2O_4\,\overset{\mathrm{VI}}{X}$$

The formulæ of these six oxides and of the corresponding acids occur more frequently and are of greater importance than any others which the pupil will encounter during his study of the not-metals. The addition of oxides of other metals besides that of hydrogen to the anhydrides, must necessarily produce reactions similar to those we have just considered.

CHAPTER XIX.

THE COMPOUNDS OF CHLORINE WITH OXYGEN, AND WITH OXYGEN AND HYDROGEN.

Chlorine forms the following compounds with oxygen and with oxygen and hydrogen:

1.	$Cl_2 O$, chlorine monoxide,	$HO Cl$, hypochlorous acid,	1.
2.	$Cl_2 O_3$, chlorine trioxide,	$HO_2 Cl$, chlorous acid,	2.
3.	$Cl O_2$, chlorine dioxide,	$HO_3 Cl$, chloric acid,	3.
		$HO_4 Cl$, perchloric acid,	4.

The first and second of the oxides are respectively the anhydrides of hypochlorous acid and of chlorous acid, the third does not form any corresponding acid.* The anhydrides of the third and fourth acids are not known, wherever an attempt is made to isolate them, complete decomposition takes place. The formulæ of the compounds would be $Cl_2 O_5$ and $Cl_2 O_7$ were they capable of existence.

Where there are four acids containing oxygen and derived from the same element, the nomenclature given in the following table has been adopted, beginning with the one containing least oxygen, we have:

1. Prefix *hypo*—termination in—*ous*.
2. No prefix— " "—*ous*.
3. No prefix— " "—*ic*.
4. Prefix *per*— " "—*ic*.

Where but two acids are known, the nomenclature is the same as under 2, and 3.

Salts derived from an acid terminating in —ous, have their names end in —ite, those from an acid terminating in —ic, in —ate. The prefix in the name of the acid is always retained in the name of the salt. The salts obtained from the above acids by replacing the hydrogen with some other metal would consequently be named as follows, with potassium as the metal:

---

*On being passed into a solution of potassium hydroxide it forms potassium chlorite, $K Cl O_2$ and potassium chlorate $K Cl O_3$.

1. $KO\ Cl$, potassium hypochlorite,
2. $KO_2\ Cl$, potassium chlorite,
3. $KO_3\ Cl$, potassium chlorate,
4. $KO_4\ Cl$, potassium perchlorate.

Where there are but two acids the nomenclature is the same as under 2, and 3.

The oxides of chlorine are all unstable, some of them even extremely explosive, so that chlorine and oxygen cannot be caused to unite directly. In this case the product of the union of two very similar elements is most unstable in its nature, a circumstance certainly not unexpected, for oxygen and fluorine, which resemble each other even more than do oxygen and chlorine, are incapable of combination. One might be tempted from such a circumstance to argue that not-metals which most resemble each other would have the least chemical affinity; but this is true only in a very few cases. The oxides of sulphur and phosphorus, for instance, are extremely stable bodies; the different halogenes can in some instances combine with each other; while the existence of molecules such as those of chlorine and hydrogen, shows us that even the atoms of the same element may be most firmly united. Any attempts to generalize regarding the relative stability of these oxides are at the present time premature.

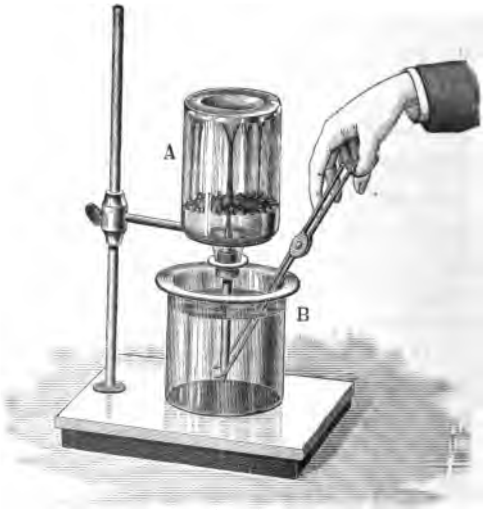


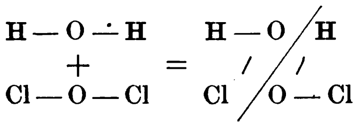
FIGURE 19.

Chlorine monoxide is not of itself important, but the acid formed from it by the addition of water is of the greatest commercial value;

its salts, more especially that of calcium, being the compounds most often used for the purpose of bleaching. The monoxide can be prepared by passing chlorine over mercuric oxide.

$$HgO + 4\,Cl = HgCl_2 + Cl_2O.$$

It is a reddish-yellow gas with a penetrating odor resembling that of chlorine. At low temperatures it is condensed to a bright red liquid which boils at 5° centigrade. It has a specific gravity, air being 1, of 3.00, hydrogen being 2, of 86.4. Its molecular weight is therefore 86.9, its formula Cl_2O. It gradually dissolves in water, forming an orange colored solution which contains hypochlorous acid:



The salts derived from hypochlorous acid are easily prepared; they are really of greater importance, and more stable than is the acid itself.

In 1788 Berthollet discovered that a bleaching solution could be prepared by passing chlorine into a solution of alkali. He at once attempted to utilize his discovery commercially, and so established a factory at Javelles, where bleaching water was prepared by passing chlorine into a solution of potashes (potassium carbonate), this solution then contained hypochlorous acid and was called *eau de Javellès*. At a later date, lime took the place of potashes and the resulting bleaching powder became known as chloride of lime.

If chlorine is passed into a solution of potassium hydroxide the first product will necessarily be potassium chloride, because of the great chemical affinity between the metal and the not-metal, therefore:

$$K — O — H + Cl = KCl + — O — H.$$

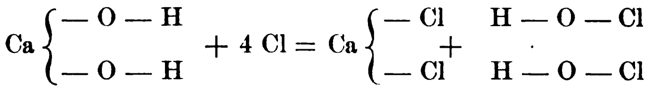
The group $— O — H$, is however unsaturated, so that it can unite with another atom, in this case with one of chlorine, $H — O — + Cl = H — O — Cl$. The first products obtained by passing chlorine into a solution of potassium hydroxide would therefore be potassium chloride and hypochlorous acid. Now potassium hydroxide is a base, therefore with hypochlorous acid, it will form a salt, (potassium hypochlorite) and water, as follows:

$$KOH + HOCl = KOCl + H_2O.$$

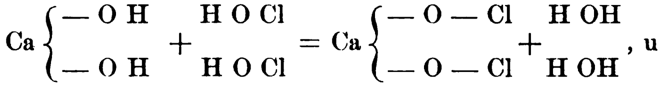
As a consequence the ultimate products of the action of chlorine upon potassium hydroxide are potassium chloride, potassium hypochlorite and water. The entire change is summed up in the following reaction:

$$2KOH + 2Cl = KCl + KOCl + H_2O.$$

If instead of potassium hydroxide, calcium hydroxide had been used, calcium chloride, calcium hypochlorite and water would be produced; the reaction wonld be modified by the bivalence of the atoms of calcium, which have twice the capacity for replacing hydrogen in acids than those of potassium possess. The reaction is therefore as follows:

1.  and

$$Ca\begin{cases}-O-H\\-O-H\end{cases} + 4\,Cl = Ca\begin{cases}-Cl\\-Cl\end{cases} + \begin{matrix}H-O-Cl\\H-O-Cl\end{matrix}$$

2. , uniting

$$Ca\begin{cases}-O\,H\\-O\,H\end{cases} + \begin{matrix}H\,O\,Cl\\H\,O\,Cl\end{matrix} = Ca\begin{cases}-O-Cl\\-O-Cl\end{cases} + \begin{matrix}H\,OH\\H\,OH\end{matrix}$$

1 and 2, we have,

$$2\,Ca\,(OH)_2 + 4\,Cl = Ca\,Cl_2 + Ca\,(O\,Cl)_2 + 2\,H_2\,O^{*}$$

A moderate heat changes hypochlorites into chlorates; therefore, the above reactions must be performed in the cold; the one using potassium hydroxide only with dilute solutions. The hypochlorites bleach because. when acidified, they liberate chlorine. The first change upon addition of acids is the production of hypochlorous acid, as follows:†

a. $K\,O\,Cl + H\,Cl = K\,Cl + H\,O\,Cl,$

b. $2\,K\,O\,Cl + H_2\,S\,O_4 = K_2\,S\,O_4 + 2\,H\,O\,Cl,$

c. $Ca\,(O\,Cl)_2 + 2\,H\,Cl = Ca\,Cl_2 + 2\,H\,O\,Cl.$

This portion of the reaction is like the formation of hydrochloric acid from the chlorides. However, hypochlorous acid is unstable and breaks down as follows:

$$H\,O\,Cl = H\,Cl + O,$$

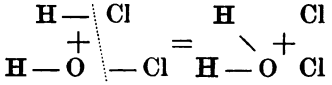
---

* There is some reason to suppose that chloride of lime contains the compound $Ca\begin{smallmatrix}-Cl\\-O\,Cl\end{smallmatrix}$, a substance which would be partly chloride and partly hypochlorite, the relative proportions of chloride and hypochlorite would remain the same as that given above, for $2\,Ca\begin{smallmatrix}-Cl\\-O\,Cl\end{smallmatrix}$ would contain the same percentage of calcium, chlorine and oxygen as $Ca\,Cl_2 + Ca\,(OCl)_2$.

† A solution of hypochlorous acid in water may, if dilute, be kept for some time.

and hydrochloric acid, in the presence of nascent oxygen, forms chlorine and water (see pages 58, 70); so that if hydrochloric acid has been used to liberate hypochlorous acid, chlorine, and not oxygen, will be set free:

$$\text{d. } H\,O\,Cl + H\,Cl = H_2\,O + 2\,Cl;$$



$$\begin{array}{cccccc} H- & Cl & & H & & Cl \\ + & & = & & \diagdown & + \\ H-O & -Cl & & H-O & & Cl \end{array}$$

Now, a chloride is always formed simultaneously with hypochlorite when chorine acts upon bases such as potassium or calcium hydroxide; so that where sulphuric acid is employed to liberate hypochloric acid the following changes take place:

$$K\,O\,Cl + K\,Cl + H_2\,S\,O_4 = K_2\,S\,O_4 + H\,Cl + H\,O\,Cl;$$
$$Ca\,(O\,Cl)_2 + Ca\,Cl_2 + 2\,H_2\,S\,O_4 = 2\,Ca\,SO_4 + 2\,H\,Cl + 2\,H\,O\,Cl,$$

and then the hypochlorous acid and hydrochloric acid which are produced can react as in equation d; the complete change would therefore be represented by the equations:

$$K\,O\,Cl + K\,Cl + H_2\,S\,O_4 = K_2\,S\,O_4 + H_2\,O + 2\,Cl;$$
$$Ca\,(O\,Cl)_2 + Ca\,Cl_2 + 2\,H_2\,S\,O_4 = 2\,Ca\,S\,O_4 + 2\,H_2\,O + 4\,Cl.$$

Chlorine, consequently, is liberated when hydrochloric or sulphuric acid is added to a hypochlorite; and the hypochlorites exercise their bleaching action by means of that element.

Hypochlorous acid is unknown in a pure state, but its solution can be prepared by passing the anhydride $Cl_2\,O$ into water, or better still, by suspending oxide of mercury in water and then subjecting this to the action of chlorine, by which means the formation of the anhydride is avoided. Concentrated solutions of hypochlorous acid possess the odor of chlorine and disintegrate in the dark, although they do so more rapidly in the daylight. If the acid is quite dilute it is much more stable, and can then even be distilled without great decomposition. A solution of hypochlorous acid is an energetic oxidizer; we have seen that hydrochloric acid is changed to chlorine by it, and other hydrogen compounds are similarly affected. Hydrogen sulphide, for instance, is affected by it as follows:

$$H_2S + HO\,Cl = S + H_2O + H\,Cl.$$

Vegetable dyes, such as litmus and indigo, are instantly bleached even by dilute solutions of the acid, and many other organic substances are destroyed by it, so that it is much used for bleaching cotton and linen goods. With silks and woolens it is useless, for these it colors yellow.

The most stable acids of hydrogen, oxygen and chlorine are those containing the most oxygen, and the same is true of the corresponding salts, so that hypochlorous acid and the hypochlorites will tend to change into compounds containing more oxygen; one portion of the salt or acid being oxidized at the expense of the other. As a consequence a potassium hypochlorite solution forms potassium chlorate when heated to boiling:

$$3\ K\,Cl\,O = K\,Cl\,O_3 + 2\ K\,Cl, \text{ or,}$$

$$\begin{array}{ccl} K\,Cl\,O & & \underline{K\,Cl}/O \\ + & & \\ K\,Cl\,O & = & K\,Cl\ \ O \\ + & & \\ K\,Cl\,O & & \overline{K\,Cl}\backslash O \end{array}$$

Now, $2\ K\,O\,H + 2\ Cl = K\,Cl + K\,Cl\ O + H_2\,O$, therefore:

1. $6\ K\,OH + 6\ Cl = 3\ K\,Cl\,O + 3\ K\,Cl + 3\ H_2\,O.$

When the solution is hot and concentrated,

2. $3\ K\,Cl\,O = 2\ K\,Cl + K\,Cl\,O_3;$

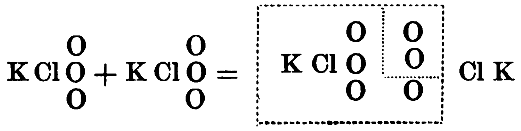
therefore when chlorine is passed into potassium hydroxide solution under those conditions the result, combining equations 1 and 2, is as follows:

$$6\ K\,OH + 6\ Cl = 5\ K\,Cl + K\,Cl\,O_3 + 3\ H_2\,O.$$

In a similar way the solution of calcium hypochlorite changes to to the chlorate of calcium on heating. Potassium chlorate is much less soluble than is calcium chlorate, so that potassium chlorate can also be prepared by adding the solution of a potassium salt to a solution containing calcium chlorate, this method is the one used for preparing the salt on a large scale:

$$Ca\ (Cl\,O_3)_2 + 2\ K\,Cl = 2\ K\,Cl\,O_3 + Ca\,Cl_2.$$

The chlorates, when heated to a temperature cousiderably higher than that required to effect the change from hypochlorites to chlorates, yield oxygen and are transformed into a mixture of chloride and perchlorate, one portion of the salt being oxidized at the expense of the other:



$$\mathrm{K\,Cl}\overset{O}{\underset{O}{O}} + \mathrm{K\,Cl}\overset{O}{\underset{O}{O}} = \boxed{\mathrm{K\,Cl}\overset{O}{\underset{O}{O}}\ \boxed{\overset{O}{\underset{O}{O}}}}\ \mathrm{Cl\,K}$$

$$\mathrm{K\,Cl\,O_3} + \mathrm{K\,Cl\,O_3} = \mathrm{K\,Cl\,O_4} + \mathrm{K\,Cl} + 2\mathrm{O}.^*$$

Finally, as potassium perchlorate is not able to take up more oxygen, the salt breaks down into potassium chloride and oxygen:

$$\mathrm{K\,Cl\,O_4} = \mathrm{K\,Cl} + 4\,\mathrm{O}.$$

When potassium chlorate is heated the salt melts at a moderate temperature, when the latter is increased oxygen begins to pass off; the salt again solidifies when it has canged completely to a mixture of the chloride and perchlorate; finally it once more melts at almost a red heat and then the potassium perchlorate parts with all of its oxygen, leaving potassium chloride in the flask. (See page 19 and foot note).

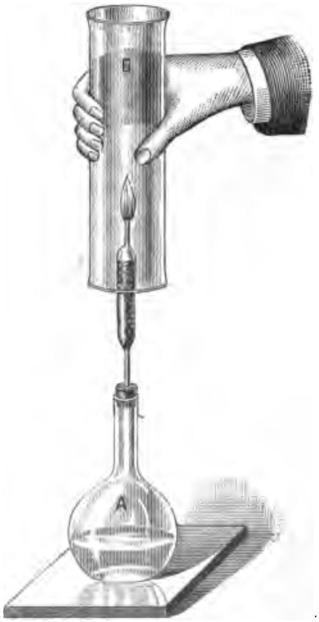


FIGURE 20.

The chlorates, especially that of potassium, are but little inferior in commercial importance to the hypochlorites. They are used chiefly for their oxidizing powers, while potassium chlorate is also of medicinal value. In using a chlorate, care must be taken not to have the salt mixed with any substance easily oxidized; very serious explosions have, for instance, resulted from grinding potassium chlorate and sugar in the same mortar. Specimens of chlorate to be used for pre-

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[*] More complicated equations are frequently given for this reaction but, although there is some variation in the amount of oxygen formed, and in the relative proportions of potassium chloride and of perchlorate left in the flask, yet the probability seems to be that in the great majority of cases the simplest equation, which is that given above, is realized.

paring oxygen should always be first tested on a small scale, in order to insure their safety. A demonstration of these facts is readily supplied by rubbing a trace of potassium chlorate over a very small bit of sulphur in a rough mortar, or by mingling some powdered chlorate with sulphide of antimony, by means gently brushing the two substances together with a feather; when the mixture is struck with a glass rod a sharp explosion will result.* The commercial application of potassium chlorate lies chiefly in the preparation of fire works and of explosive matches.

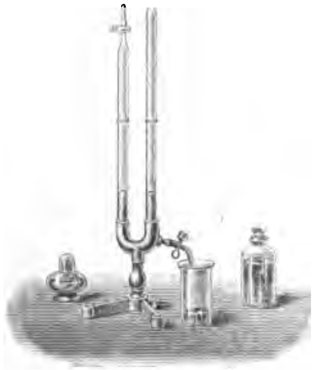
FIGURE 21.

Potassium perchlorate is very nearly insoluble in cold water and therefore is of value in qualitative analysis, and because of its greater stability it is sometimes used in pyrotechnics in place of potassium chlorate.

Chloric and perchloric acids are more easily decomposed by heat than are their salts, but they possess greater stability than do hypochlorous or chlorous acids. Either can be prepared according to the usual method, by the addition of sulphuric acid to the corresponding salt:

$$2\,K\,Cl\,O_3 + H_2\,SO_4 = K_2\,SO_4 + 2\,H\,Cl\,O_3.\dagger$$
$$2\,K\,Cl\,O_4 + H_2\,SO_4 = K_2\,SO_4 + 2\,H\,Cl\,O_4,$$

but they also are the products of decomposition of those chlorine acids which contain less oxygen; these, when heated, change to chloric acid, but as hydrochloric acid is formed during this change, a certain amount of chlorine must also be given off, because these powerful oxidizers always destroy such compounds of hydrogen. Chloric acid finally changes to perchloric acid upon being heated above 40°:

$$2\,H\,Cl\,O_3 = H\,Cl\,O_4 + H\,Cl + 2\,O.$$

Of course the oxygen formed by this decomposition further acts on the hydrochloric acid, forming water and liberating chlorine, so that the reaction is more complicated than the equation. Of all these acids, perchloric acid is the most stable; its aqueous solution can be distilled without decomposition so that by this means it can be separated from the sulphuric acid introduced in its preparation. It is an oily substance, and because it can be obtained in a pure state best illustrates the intense capacity for oxidation possessed by these chlorine compounds. This is shown by placing a drop of the acid upon paper or wood, for then a violent explosion ensues. The acid itself, when kept for some time, decomposes spontaneously with explosive violence.

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* Only very small quantities must be used.

† It is better to use barium chlorate, for then sulphuric acid will form insoluble barium sulphate, which can be filtered off.

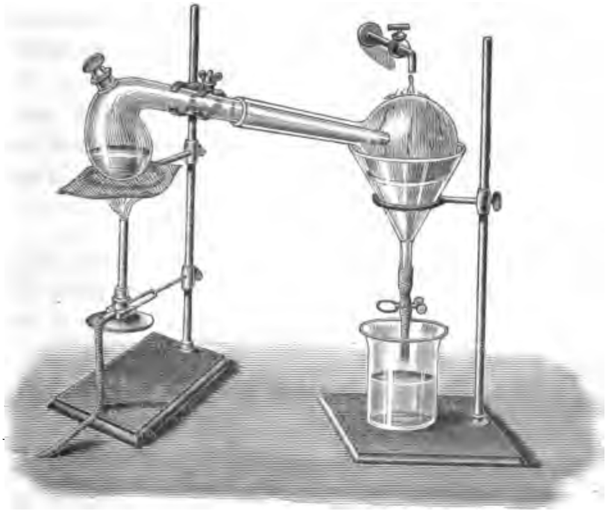


FIGURE 22.

Chlorine trioxide, chlorous acid, and chlorine dioxide are the only chlorine and oxygen compounds which remain for discussion. Chlorine trioxde, the anhydride of chlorous acid, is made by the reduction of chloric acid by means of arsenic trioxide.* The substance is a green gas with a most penetrating and irritating odor. In preparing the gas the temperature must be kept quite low, otherwise a most dangerous explosion may result. It forms a dark-brown liquid at the temperature of snow and salt, and this liquid decomposes even in the dark. When dissolved in water, chlorine trioxide forms chlorous acid:

---

* $2 H Cl O_3 + As_2 O_3 = H_2 O + Cl_2 O_3 + As_2 O_5$. The $H Cl O_3$ can be formed by adding nitric acid to potassium chlorate: $K Cl O_3 + H NO_3 = K NO_3 + H Cl O_3$; when potassium nitrate and chloric acid result.

$$Cl_2\,O_3 + H_2\,O = 2\,H\,Cl\,O_2.$$

The solution is a powerful bleaching and oxidizing agent. On standing it changes to chloric acid and hydrochloric acid, which latter is further oxidized to chlorine and water. The acid neutralizes bases very slowly, the salts formed by such neutralization are called chlorites and are powerful oxidizers; many of them change to the chlorates quite readily, the nature of this alteration being, in principle, the same as that accompanying the transformation of chlorates into perchlorates. Potassium chlorite is converted into the chlorate at 160°.

Chlorine dioxide is an unstable, greenish-yellow gas, formed when concentrated sulphuric acid acts upon potassium chlorate. In this reaction we might expect the production of chloric anhydride:

$$2\,H\,Cl\,O_3 - H_2\,O = Cl_2\,O_5;$$

for the concentrated acid would remove water from chloric acid. This is not the case, however, for the chlorine pentoxide which might result is incapable of existence, so that a part of its oxygen is used in oxidizing chloric acid to perchloric acid:

$$H\,Cl\,O_3 + Cl_2\,O_5 = H\,Cl\,O_4 + 2\,Cl\,O_2.$$

The gas is a most powerful oxidizing agent, combustible substances burn in it with explosive violence, as may be shown by mixing some potassium chlorate with sugar* and adding a drop of concentrated sulphuric acid, when the mass will instantly take fire. If a little chlorate of potassium is placed in a deep glass, covered with water, a small piece of phosphorus dropped in and then sulphuric acid carefully poured directly on the salt by means of pipette the combustion of phosphorus by means of the chlorine dioxide liberated can be seen to take place under the surface of the water. If the gas is warmed, a dangerous explosion results, so that care must be taken never to warm a mixture of sulphuric acid and potassium chlorate. The specific gravity of the gas shows that it has the formula $Cl\,O_2$, so that if we consider oxygen as bivalent, chlorine is quadrivalent in this compound.

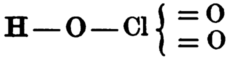
---

* Do not rub in a mortar.

The generally accepted theory regarding the constitution of these acids is as follows. The hydrogen atom is not attached to chlorine, but to oxygen, forming a part of the hydroxyle group; and this hydrogen atom is replaced by metals when the salts are formed:

$$H-O-Cl$$

Hypochlorous acid.

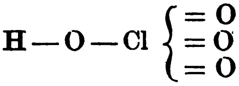


$$H-O-Cl\left\{\begin{matrix}=O\\=O\end{matrix}\right.$$

Chloric acid.

$$H-O-Cl=O$$

Chlorous acid.



$$H-O-Cl\left\{\begin{matrix}=O\\=O\\=O\end{matrix}\right.$$

Perchloric acid.

The existence of the hydroxyle group in acids containing oxygen has already been discussed. (See pages 110, 111, 112).

The most striking chemical characteristics of the acids composed of chlorine, oxygen and hydrogen, are their intense power of oxidizing, their extreme instability and the tendency which those with a lesser amount of oxygen have to change into those with a greater. Although the salts are as a rule more stable, they nevertheless display similar properties.

CHAPTER XX.

COMPOUNDS OF BROMINE AND OF IODINE WITH OXYGEN AND HYDROGEN, THE COMPOUND OF IODINE WITH OXYGEN AND THE COMPOUNDS OF THE HALOGENES WITH EACH OTHER.

All attempts to isolate oxides of bromine have proved futile; unstable as the oxides of chlorine are, those of bromine are evidently still more so. The acids containing bromine, oxygen and hydrogen are only known in aqueous solutions; their formulæ correspond to those of the chlorine-acids, but bromous acid is unknown and the existence of perbromic acid is very doubtful. The only compounds of bromine, oxygen and hydrogen with which we have to deal are therefore hypobromous acid, $H\,Br\,O$, bromic acid, $H\,Br\,O_3$, while in addition we must discuss the salts derived from these.

Solutions of hypobromous acid in water are produced under circumstances exactly analogous to those which were observed in the preparation of hypochlorous acid; such solutions have powerful bleaching properties and are very readily decomposed even by slight warmth. When bromine is added to very dilute potassium hydroxide solution, a liquid having bleaching properties is produced; the reaction is similar to that encountered in studying the action of chlorine on a dilute and cold solution of caustic potash. (See page 115).

$$2\,K\,O\,H + 2\,Br = K\,Br + K\,O\,Br + H_2O.$$

When the potassium hydroxide solution is too concentrated, bromate of potassium is produced even at ordinary temperatures, the conversion of hypobromites into bromates being a change much more readily produced than the corresponding one with chlorine, but the principle of the action is the same:

$$6\,K\,O\,H + 6\,Br = 5\,K\,Br + K\,O_3\,Br + 3\,H_2O.^*$$

---

* It is not necessary to enter into the explanation of the course of these reactions, the pupil should undertake this by repeating the various phases given under chlorine, while substituting bromine for the latter element.

The bromate of potassium is not very soluble, so that it can be filtered from the solution containing the bromide and recrystallized from hot water; bromate of barium can be prepared in a similar manner. The latter will yield a solution of bromic acid when exactly enough sulphuric acid to form barium sulphate is added:

$$Ba(BrO_3)_2 + H_2SO_4 = BaSO_4 + 2HBrO_3.$$

The solution of bromic acid is colorless and may be concentrated by evaporating the excess of water in a vacuum, but when warmed the acid breaks down completely into bromine, oxygen and water. Naturally all of the compounds under consideration are powerful oxidizers; the bromates form very explosive mixtures with oxidizable substances, while the bromate of ammonium may even explode spontaneously.

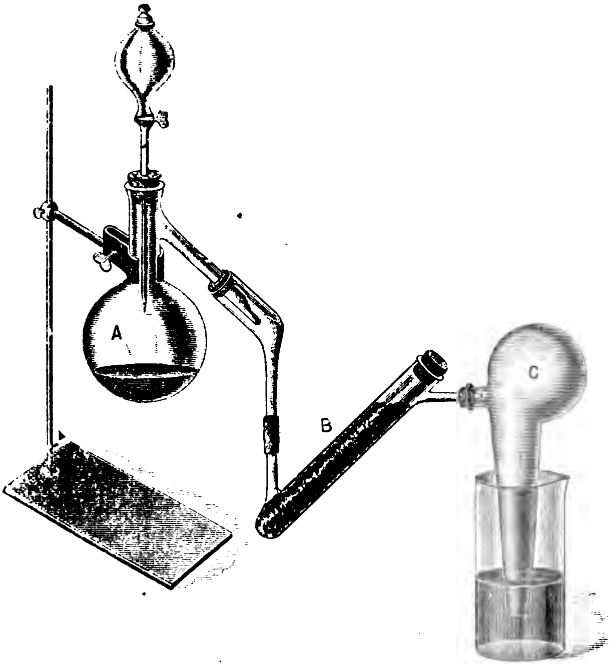


FIGURE 23.

Iodine forms the pentoxide I_2O_5 and two acids, iodic acid HIO_3

and per-iodic acid. If the anhydride of the latter acid existed, it would have the formula $I_2 O_7$, for in the previous chapter we saw that the theoretical anhydride of perchloric acid would be $\overset{\text{VII}}{Cl_2} O_7$, now by the addition of water to these anhydrides the first products would be per-iodic and perchloric acids respectively, as follows:

$$I_2 O_7 + H_2 O = 2\,HIO_4,$$
$$Cl_2 O_7 + H_2 O = 2\,H\,Cl\,O_4.$$

If we recall the structural formulæ of these acids, it seems reasonable to suppose that the oxygen atoms contained in them would be capable of adding the elements of water to form hydroxyle groups, in conformity with the tendency manifested in the production of such groups by the addition of water to the anhydrides, and in this way more complicated compounds would result:

$$X\left\{\begin{array}{l} =O \\ =O \\ =O + H\text{-}O\text{-}H = \\ -O\text{-}H \end{array}\right. X\left\{\begin{array}{l} =O \\ =O + H\text{-}O\text{-}H \\ -O\text{-}H \quad\quad = \\ -O\text{-}H \\ -O\text{-}H \end{array}\right. X\left\{\begin{array}{l} =O \; + H\text{-}O\text{-}H \\ -O\text{-}H \\ -O\text{-}H \\ -O\text{-}H \quad\quad = \\ -O\text{-}H \\ -O\text{-}H \end{array}\right. X\left\{\begin{array}{l} -O\text{-}H \\ -O\text{-}H \\ -O\text{-}H \\ -O\text{-}H \\ -O\text{-}H \\ -O\text{-}H \\ -O\text{-}H \end{array}\right.$$

First acid, Second acid, Third acid, Fourth acid.

$$XO_4 H + H_2 O = X O_5 H_3 + H_2 O = X O_6 H_5 + H_2 O = X O_7 H_7.$$

With the addition of each molecule of water *one* oxygen atom of the acid can yield *two* hydroxyle groups until finally all have been converted and a complete hydroxide has been produced. This last acid is called the *normal* acid. By separating water from the normal acid the various other acids can be formed, so that in the end we arrive at an anhydride which is obviously identical with that from which we started. None of these changes involve either an oxidation or a reduction, for if such were to take place we would produce acids derived from different anhydrides in which the valence of the characterizing element would vary, therefore we can assume that in the change from the anhydride to the first acid and in the subsequent conversion of this to the normal acid, no alteration in the valence of X in the above formulæ has taken place. The process of adding water to these anhydrides is called hydration, and the acids, excepting the ones with least amount of hydrogen, are called hydrated acids. Hydrated acids occur quite frequently, but normal acids are extremely unstable, their existence even in solution is doubtful, for when a large number of hydroxyle groups are attached to the same element they will always show a great tendency to separate water; yet often the acids lying between that having the least hydrogen and the normal acid have no tendency to break down, in fact they are sometimes the only ones which we encounter. In many of the hydrated acids only a portion of the hydrogen atoms can be replaced by metals to form salts, a fact not surprising if we consider that as soon as a hydrogen atom in an acid is replaced by a more metallic element, the whole compound is rendered more positive and hence has its tendency to take up positive elements diminished. Per-iodic acid exists in the hydrated form $H_5 O_6 I$, corresponding to the third acid of the series given on the table above.

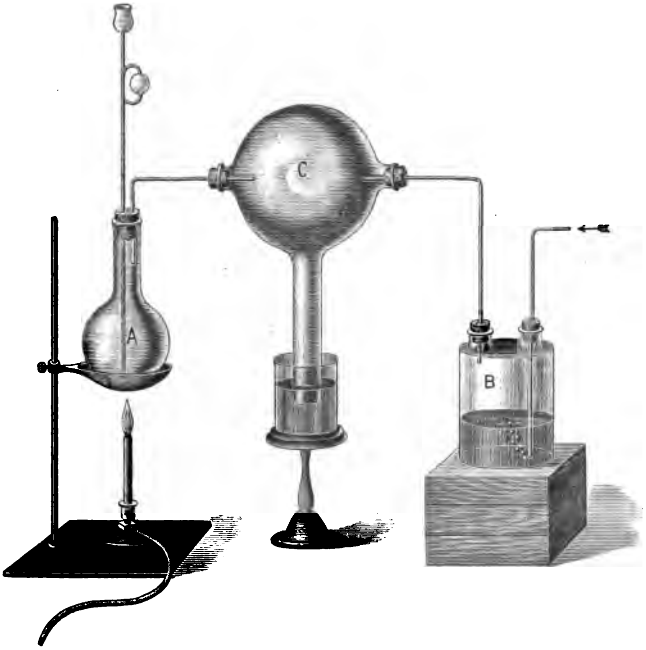


FIGURE 24.

The pentoxide of iodine forms a white powder, which melts at 300° and then instantly decomposes into oxygen and iodine; it is produced by oxidizing iodine with nitric acid or by heating iodic acid for some time at 170°. The oxides of chlorine are all endothermic substances, but 453 K are liberated in the formation of $I_2 O_5$, so that while the former compounds are explosive the latter is quite stable. From this we see that with the diminishing not-metallic character of the halogenes there appears a diminishing stability of the compounds of those elements with metals, while at the same time an increasing stability of the oxides is manifested, but when we try to draw general conclusions from these facts we must remember that the oxides of bromine are less stable than those of chlorine.

Iodic acid can be prepared by oxidizing iodine suspended in water, by means of chlorine, or by adding the anhydride, $I_2 O_5$, to water. It is a crystalline solid with powerful oxidizing properties; phosphorus and arsenic, for instance, are oxidized by it respectively to phosphoric and arsenic acids, while it even changes graphite to carbon dioxide.

The iodates are formed either by adding a base to iodic acid:

$$XOH + HIO_3, = HIO_3 + HOH,*$$

or by dissolving iodine in an alkali, a reaction the same as that which took place with chlorine or bromine:

$$6\ K\ OH + 6\ I = 5\ KI + KIO_3 + 3\ H_2\ O.$$

Iodic acid can be liberated by adding a non-oxidizable acid to the iodates. Many of the iodates form per-iodates when heated, but the latter can also be produced from the former by the addition of some oxidizer. Two of the per-iodates ($Ag\,IO_4$, $KI\,O_4$) correspond to the perchlorates in formula, but the majority of the salts of per-iodic acid are derived from the hydrated acids, for instance $Na_5\ I\ O_6$ from $H_5\ I\ O_6$ and $Ag_3\ I\ O_5$ from $H_3\ I\ O_5$. Salts of per-iodic acid in which only a part of the hydrogen atoms have been replaced by other metals are known; an example of such a salt would be $Na_2\ H_3\ IO_6$. Per-iodic can be formed from its salts by the addition of some other acid, and when separated from its solutions by slow evaporation it is a crystalline solid of the formula $H_5\ IO_6$ and is a powerful oxidizer. Other more complicated per-iodic acids and periodates exist, but for their study the pupil must be referred to some larger work.

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* It obviously makes no difference whether we write iodic acid HIO^3 or $HO^3\ I$ sulphuric acid $H_2\ O_4\ S$ or $H_2\ SO_4$, etc., except in cases where we intend to convey some idea as regards the structural formulæ of the acids, but the method of writing the formulæ of acids with the symbol of oxygen as the terminal letter is the one rendered more familiar by usage. Both systems are employed in this book.

The halogenes can form a number of compounds with each other. Three of these are produced by the union of the elements, atom for atom, they are $Br\,Cl$, bromine monochloride, an unstable liquid decomposing above 10°, $I\,Cl$, iodine monochloride, a fluid which is readily decomposed by water, and $I\,Br$, iodine monobromide, a more stable, crystalline solid. In addition to these, a solid trichloride of iodine, $I\,Cl_3$ and a liquid penta fluoride $I\,F_5$ are known. $Br\,Cl$, $I\,Cl$ and $I\,Br$ are formed by the direct union of the elements; $I\,Cl_3$ by the addition of chlorine to $I\,Cl$ and $I\,F_5$ by the action of iodine on the fluoride of silver. All of these compounds are decomposed by the addition of water, although $I\,Cl_3$ can exist provided but little water is present. The reaction with $I\,F_5$ is as follows:

$$I\,F_5 + 3\,H_2\,O = H\,IO_3 + 5\,HF.$$

Iodic acid, which is derived from an oxide, $I_2\,O_5$, in which iodine is quinquivalent, is therefore also formed from a fluoride of iodine in which the latter is likewise quinquivalent. In comparing the formulæ of $I\,Br$, $I\,Cl_3$ and $I\,F_5$ we are impressed with the fact that an atom of iodine can combine with more atoms of another halogene, the greater the difference between the atomic weights of the two uniting elements.

The following is a table of the formulæ belonging to the compounds discussed in the last two chapters:

CHLORINE.		BROMINE.	IODINE.	
Oxides $Cl_2\,O$	Acids $H\,O\,Cl$	Acids $H\,O\,Br$	Oxides ——	Acids ——
$Cl_2\,O_3$	$H\,O_2\,Cl$	——	——	——
$Cl\,O_2$	——	——	——	——
	$H\,O_3\,Cl$	$H\,O_3\,Br$	$I_2\,O_5$	$H\,O_3\,I$
	$H\,O_4\,Cl$	$H\,O_4\,Br$[*]		$H\,O_4\,I$[†]

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[*] Existence doubtful.

[†] This acid exists in its hydrated form, $H_5\,IO_6$. The stability of all of the acids and of their salts increases with increasing number of oxygen atoms. They are all powerful oxidizers.

CHAPTER XXI.

THE COMPOUNDS OF THE ELEMENTS OF THE SULPHUR FAMILY WITH OXYGEN AND WITH OXYGEN AND HYDROGEN.

Sulphur dioxide and sulphurous acid. Sulphur dioxide—Formula SO_2, *specific gravity, air* $= 1$, *is* 2.23, $H = 2$ *is* 63.90; *1 c.c. at* 0° *and .76 m pressure weighs .00286 grams.*

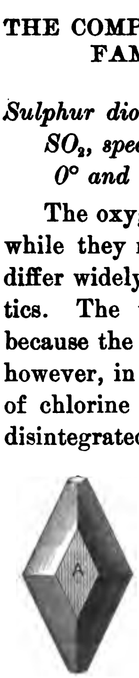


FIGURE 25.

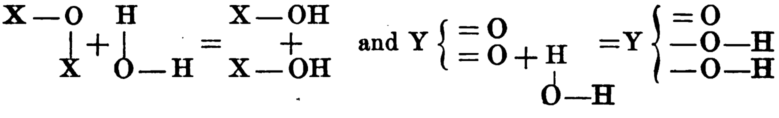
The oxygen compounds of the elements of the sulphur family, while they manifest certain resemblances to those of the halogenes, differ widely from the latter, both in their formulæ and characteristics. The two series of compounds resemble each other chiefly because the members of both are anhydrides, they differ very greatly however, in the ease with which they are decomposed. The oxides of chlorine were all explosive compounds, while that of iodine was disintegrated at 300°; on the other hand those of the elements of the sulphur family are quite stable and also have different formulæ. Thus the oxides of the halogenes (with the exception of $Cl\,O_2$) are formed by joining two atoms of such an element by means of a bivalent oxygen atom as in $Cl - O - Cl$ and $O = Cl - O - Cl = O$, while the ones of the sulphur group have no such linking, as will be seen from the formulæ of the following compounds:

$$S\left\{\begin{array}{l}=O\\=O\end{array}\right. \quad \text{and} \quad S\left\{\begin{array}{l}=O\\=O\\=O\end{array}\right.$$

This difference in the formulæ of the anhydrides produces a difference in those of the acids derived from them, for, in changing the oxides of the halogenes into acids, the water, in order to form two hydroxile groups, attacks the linking oxygen, and thus gives us acids containing but one hydrogen atom, but in

FIGURE 26.

converting the oxides of the sulphur family no such separation can take place. The following formulæ will make this more apparent (X denotes a halogene atom and Y an atom of any element of the sulphur group):



$$\begin{array}{l}X-O\\ |\\ X\end{array}+\begin{array}{l}H\\ |\\ O-H\end{array}=\begin{array}{c}X-OH\\ +\\ X-OH\end{array}\quad\text{and}\quad Y\left\{\begin{array}{l}=O\\ =O\end{array}\right.+\begin{array}{l}H\\ |\\ O-H\end{array}=Y\left\{\begin{array}{l}=O\\ -O-H\\ -O-H\end{array}\right.$$

$$X_2O + H_2O = 2X\ OH \quad \text{and} \quad YO_2 + H_2\ O = Y\,O_3\ H_2$$

The above makes it plainly evident that while the first acid derived from any of the oxides of the halogenes must contain one hydrogen atom, those of the sulphur group must contain two. As a general rule, the most important acids in any chemical family have as many replaceable hydrogen atoms as are contained in the corresponding hydrogen compounds, for instance, $H\,Cl$ and $H\,Cl\,O_3$, $H\,I$ and $H\,IO_3$, $H_2\,S$ and $H_2\,SO_4$, $H_2\,Se$ and $H_2\,Se\,O_3$. All of the hydrated acids must bear a simple relationship to these, for they are simply formed therefrom by the addition of water. Subsequently we will see that the same rule appertains to the nitrogen family,

The elements of the sulphur family form the following oxides and acids:

$S\,O_2$ sulphur dioxide $+ H_2\,O = H_2\,SO_3$ sulphurous acid.
$S\,O_3$ sulphur trioxide $+ H_2\,O = H_2\,SO_4$ sulphuric acid.
$Se\,O_2$ selenium dioxide $+ H_2\,O = H_2\,Se\,O_3$ selenious acid.
$Te\,O_2$ Tellurium dioxide $+ H_2\,O = H_2\,Te\,O_3$ Tellurous acid.
$Te\,O_3$ Tellurium trioxide $+ H_2\,O = H_2\,Te\,O_4$ Telluric acid.

Two oxides, $S_2\,O_3$ and $S_2\,O_7$, have also been made, while a number of sulphur acids of less importance than the above exist. Mention of these will be made at the proper time. All the elements of the sulphur group, on burning in air or oxygen, form the dioxides, and these can be converted into the trioxides by oxidation, excepting in the case of selenium, the trioxide of which has never been prepared.

The natural occurrence of sulphur dioxide is limited to the gases which escape from the craters of volcanoes, but as sulphur is generally found in the coals used as fuel, sulphur dioxide must be a product of their combustion, and hence occurs in minute traces in the atmosphere of cities, although, being moist, it is rapidly oxidized.

The history of sulphur dioxide is as ancient as that of sulphur itself, for as it is produced by the combustion of the latter, its properties could not fail to become an object of interest. The Romans were well acquainted with the disinfecting powers of burning sulphur and used it in cleansing their wine-skins; sulphur dioxide was confounded with sulphuric acid by the alchemists; Stahl first proved its individuality; Priestley obtained it pure by collecting over mercury and Lavoisier explained its composition.

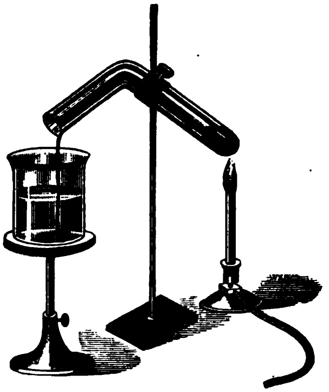


FIGURE 27.

Sulphur dioxide can be formed either by oxidizing sulphur or by deoxidizing sulphuric acid. With the first method we are already acquainted, for we saw that sulphur or combustible substances containing sulphur, yielded sulphur dioxide in burning; the second method is best employed in preparing the gas for laboratory use. Substances, such as charcoal, sulphur and some of the metals, will reduce sulphuric acid while they themselves become oxidized. If charcoal is heated with sulphuric acid carbon dioxide and sulphurous acid are produced:

$$2\,H_2SO_4 + C = CO_2 + 2\,H_2SO_3,$$

but the latter, being an acid the anhydride of which is a gas, breaks down into water and that anhydride:—

$$H_2SO_4 = H_2O + SO_2.$$

Sulphur acts in a manner similar to charcoal, with the difference that with it only sulphur dioxide can be formed:—

$$2\,H_2SO_4 + S = SO_2 + 2\,H_2SO_3 \text{ and } 2\,H_2SO_3 = 2\,H_2O + 2\,SO_2,$$

so that:—

$$2\,H_2SO_4 + S = 3\,SO_2 + 2\,H_2O.$$

Better than either of these methods is the preparation by means of copper and sulphuric acid. Cold sulphuric acid has very little action on copper, but if copper shavings are heated with sulphuric acid, sulphur dioxide will be given off [42]. Some little doubt exists as to the mechanism of this reaction. One explanation which has been offered is as follows. When dilute sulphuric acid acts on zinc, hydrogen is produced:

$$Zn + H_2\,SO_4 = Zn\,SO_4 + 2\,H,$$

but if the sulphuric acid is hot and concentrated, not hydrogen, but sulphur dioxide is formed. It is therefore reasonable to suppose that the first result of the contact of zinc and sulphuric acid always is the liberation of hydrogen, but when the acid is hot and concentrated the conditions are so altered that it will give up its oxygen very readily. The hydrogen which is being generated would then form water with the oxygen, so that sulphurous acid would be set free:

1. $Zn + H_2\,SO_4 = Zn\,SO_4 + 2\,H$
2. $2\,H + H_2\,SO_4 = 2\,H_2\,O + SO_2$, combining 1 and 2 we have,
3. $Zn + 2\,H_2\,SO_4 = Zn\,SO_4 + 2H_2\,O + SO_2$.

Now, although copper produces no hydrogen with sulphuric acid, yet it can be conjectured that the reaction takes place in a manner similar to that given above, substituting copper for zinc. There is strong reason to suppose, however, that when metals produce sulphur dioxide from sulphuric acid, they act exactly as do carbon or sulphur, by removing oxygen without having to call in the aid of hydrogen:

$$H_2\,SO_4 + Cu = H_2\,SO_3 + Cu\,O.$$

The copper oxide formed, being a base, would dissolve in sulphuric acid, forming copper sulphate and water:

$$Cu\,O + H_2\,SO_4 = Cu\,SO_4 + H_2\,O,$$

so that the entire reaction would be:

$$2H_2\,SO_4 + Cu = Cu\,SO_4 + SO_2 + 2\,H_2\,O.$$

Reactions of this kind are, however, not as simple as has generally been supposed.

Another method quite frequently employed in the preparation of sulphuric acid is by an addition of an acid to a sulphite, thus:

$$Na_2SO_3 + 2\,H\,Cl = 2\,Na\,Cl + H_2\,SO_3.$$
$$Na_2\,SO_3 + H_2\,SO_4 = Na_2\,SO_4 + H_2\,SO_3,$$

the sulphurous acid so formed then breaks down into sulphur dioxide and water. This way of preparing sulphur dioxide is often very convenient, for the apparatus which was employed in the production of hydrochloric acid can be used.

Sulphur dioxide is a colorless gas with the familiar odor of a burning sulphur match. The application of the moderate cold of salt and snow changes it to a clear liquid, which boils at —10°.[43] If this liquid is evaporated rapidly under the air pump, the temperature sinks to — 68°, while the liquid freezes at — 76°. Sulphur dioxide is poisonous; when it is present in small quantities it causes irritation of the throat and violent coughing, in larger quantities hemorrhages from the lungs, mouth and nose occur. Workmen who are continually exposed to the gas are affected with loss of appetite and headache. Vegetation is destroyed by sulphur dioxide so that in many places very stringent laws are passed regulating the working of factories, from the chimneys of which sulphur dioxide escapes. Sulphur dioxide is not combustible, a fact which is self-evident when we consider that it is the only compound of sulphur ever formed by burning that element in the air; it is an extremely stable body and hence will not support combustion, in fact only in a few instances, such as in its action on sulphuretted hydrogen, does it appear as an oxidizer. (See page 88.)

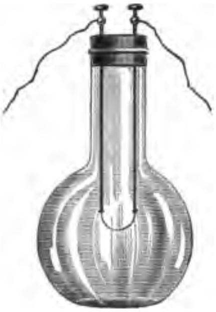


FIGURE 28.

When sulphur burns in oxygen no change of volume of the gas occurs, this phenomenon which is like that we observed in the decomposition of sulphuretted hydrogen by means of a hot iron, for that also took place without alteration of volume. The explanation is the same in both cases, for in the one, each molecule of $H_2 S$ yields a corresponding molecule of hydrogen, while the volume of solid sulphur produced need not be taken in consideration; in the other each molecule of oxygen takes up an atom of sulphur to produce a molecule of SO_2, so that any number of molecules of $H_2 S$ would yield the same number of molecules of H_2 and any number of molecules of O_2 would yield the same number of SO_2.

Sulphur dioxide can, under proper conditions, readily add oxygen to form sulphur trioxide; so for instance, sulphur trioxide is produced by passing a mixture of sulphur dioxide and oxygen through a heated tube containing a piece of spongy platinum, or when sulphur dioxide is exposed to the action of ozone. In the same way the gas can add chlorine, for sulphur dioxide and chlorine mixed and placed in the sunlight produce sulphuryl chloride, $SO_2\,Cl_2$, a compound which is of considerable importance to us theoretically:

$$SO_2 + 2\,Cl = SO_2\,Cl_2.$$

Sulphur dioxide is quite soluble in water, one volume of that liquid absorbs 45 volumes of the gas at ordinary temperatures; the solution has the odor and characteristics of sulphur dioxide and it presumably contains sulphurous acid, which is chemically a much more reactive substance than the gaseous anhydride, it readily absorbs oxygen from the atmosphere and therefore, if left exposed for any considerable length of time, will contain nothing but sulphuric acid. It is consequently self-evident that oxidizing agents such as chlorine, bromine or nitric acid will change sulphurous acid to sulphuric acid

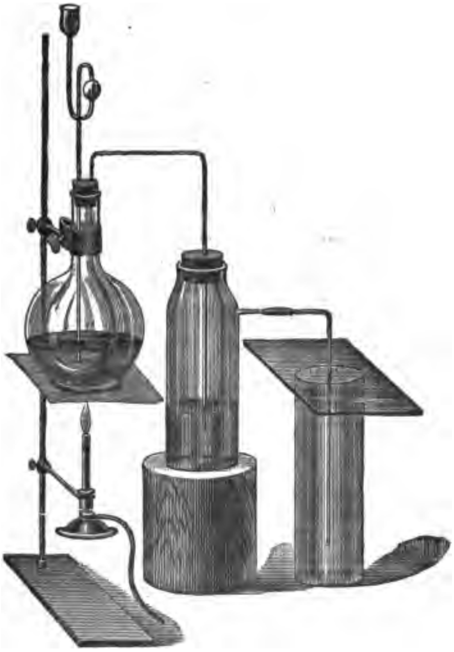


FIGURE 29.

with the greatest ease. Two atoms of chlorine or bromine produce one atom of oxygen from water:—

$$H_2\,O + 2\,Cl = 2\,H\,Cl + O,$$

and one formula weight of sulphurous acid requires one atom of oxygen to change it to sulphuric acid:—

$$H_2\,SO_3 + O = H_2\,SO_4,$$

therefore

$$H_2\,SO_3 + 2\,X + H_2\,O = H_2\,SO_4 + 2\,HX$$

where X is used to designate the halogene. The oxidation of sulphurous acid with nitric acid and the oxides of nitrogen, which is used in one of the most important commercial processes known—namely in the preparation of sulphuric acid, will be discussed in connection with that substance. Sulphurous acid is one of the favorite reducing agents in the laboratory and we will frequently have occasion to refer to it in that capacity.

When heated in a sealed tube, sulphurous acid changes to sulphuric acid and sulphur:—

$$3\,H_2\,SO_3 = 2\,H_2\,SO_4 + H_2\,O + S$$

and in the same way the sulphites, when heated, always form sulphates by using all of their oxygen for this purpose, for instance:—

$$4\,Na_2\,SO_3 = 3\,Na_2\,SO_4 + Na_2\,S.$$

These reactions remind us most forcibly of the similar ones which took place with the oxygen acids of the halogenes, for those acids and salts containing the most oxygen were also the most stable.

Acids which contain one atom of hydrogen replaceable by metals are called *unibasic*, those with two, *dibasic*, those with three, *tribasic*, those with four, *quadribasic*, and so on, while all acids with more than one replaceable hydrogen atom are *polybasic*, so that sulphurous acid is a dibasic acid. We are acquainted with two series of salts derived from dibasic acids, accordingly as the metal replaces one or both atoms of hydrogen. If we designate a univalent metal by M, then these salts of sulphurous acid would be $M\,HSO_3$ and $M_2\,SO_3$ respectively, if M′ denotes a divalent metal, then the formulæ are:—

$$\begin{array}{l} H \\ M' \\ H \end{array}\begin{array}{l} >SO_3 \\ >SO_3 \end{array} = M'\,(H\,SO_3)_2 \text{ and } M'\,SO_3.$$

Salts formed by replacing one atomof hydrogen in an acid by a metal, are called primary, those by replacing two, secondary, those by replacing three, tertiary and so on, so that $Na\ H\ SO_3$ would be primary, and $Na_2\ SO_3$ secondary sodium sulphite*. When a base acts upon sulphurous acid we can consider the first reaction to be as follows:—

$$S\left\{\begin{array}{l}—O—H + M\,O\,H\\ =O\\ —O—H\end{array}\right. = S\left\{\begin{array}{l}—O—M + H_2\,O\\ =O\\ —O\,H\end{array}\right.$$

$$SO_3\,H_2 + M\,O\,H = SO_3\,H\,M + H_2\,O.$$

Sulphurous acid + a base = a primary sulphite + water.

More of the base acting on the primary salt would then produce the secondary:—

$$S\left\{\begin{array}{l}—O—M\\ =O\\ —O—H + M\,O\,H\end{array}\right. = S\left\{\begin{array}{l}—O—M\\ =O\\ —O—M + H_2\,O.\end{array}\right.$$

$$SO_3\,MH + MOH = SO_3\,M_2 + H_2\,O.$$

Primary sodium sulphite + a base = secondary sodium sulphite + water.

Adding a base to a primary salt will therefore produce a secondary one; and inversely, adding more of the acid to the secondary salt will produce the primary one:

$$SO_3\,M_2 + H_2\,SO_3 = 2\,SO_3\,MH.$$

Salts containing hydrogen which has not been replaced by metals are frequently called *acid* salts, and those which have exchanged all of their hydrogen, *neutral*, salts, but such designations are frequently misleading, for we are acquainted with salts of the former class, such as the primary carbonate of sodium, $Na\,H\,CO_3$, having an alkaline reaction, while in some cases those of the latter are acid toward litmus, as is the case with aluminium sulphate, $Al_2\ (SO_4)_3$. Where a metal like sodium, which has most pronounced metallic properties, replaces the hydrogen of a weak acid, the resulting salt is apt to have an alkaline reaction and conversely, where a metal which is not strongly characterized, as is aluminium, is found forming a salt

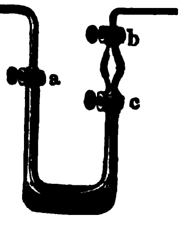


FIGURE 30.

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*Sometimes called acid and neutral sodium sulphite while $Na\ HSO_3$ is also sometimes called sodium bisulphite.

with a strong acid, then the reaction of the salt will probably be acid. But what is a weak and what is a strong acid? The question is much easier to ask than to answer, but the following must at present be taken as coming nearest the truth. When an acid acts on a salt it partially expells the acid of the latter and unites with the base, and if equivalent quantities are taken, the distribution ratio of the base is a measure of the affinity. By equivalent quantities we mean the amount in grams expressed by the formula weights. Thus equivalent quantities of sodium chloride and sulphuric acid would be:

$NaCl$, formula weight $23 + 35.5 = 58.5$.
H_2SO_4 " " $2 + 32 + (4 \times 16) = 98$

Equivalent quantities:

58.5 grams sodium chloride and 98 grams sulphuric acid, for $NaCl + H_2SO_4$.

"Daily experience in the laboratory teaches us that the affinity of acids for bases is of such a nature as to appear a specific property of the acids. When we say that carbonic acid is a weak acid and sulphuric acid a strong one, we do not thereby mean that it is so with respect to this or the other base, but that it is so in general."* Any metal replacing the hydrogen of acetic acid, for instance, will be more feebly united in the resulting salt than it would be with sulphuric acid, no matter if we compare the salts of the intensely metallic potassium or of the weakly metallic aluminium. If we mix sodium chloride and nitric acid in aqueous solution and in equivalent quantities, the following changes will take place, until an equilibrium is reached:

$$NaCl + HNO_3 = NaNO_3 + HCl \quad \text{and}$$
$$NaNO_3 + HCl = NaCl + HNO_3$$

So that $NaCl$, HNO_3, $NaNO_3$ and HCl will all be present. Now, the two salts, $NaCl$ and $NaNO_3$, will be formed in equal quantities, so that hydrochloric and nitric acids are acids of about the same strength. If, on the other hand, we mix sodium chloride with sulphuric acid, about two-thirds of the metal will remain in sodium chloride, while one-third will go to form sodium sulphate, and accordingly, sulphuric acid would be a weaker acid than hydrochloric acid, contrary to what is generally supposed. The distribution ratio of the metal used in the above reactions would therefore be as 1:1 with nitric and hydrochloric acids and as 3:2 with hydrochloric and sulphuric acids. This conclusion, at first sight, seems very strange if we remember that when tolerably concentrated sulphuric acid is added to sodium chloride or sodium nitrate, sodium sulphate is formed and either hydrochloric acid or nitric acid are given off, but we must consider, that after mixing salts and acids, the least volatile acid will, upon heating, finally expel the more volatile ones from their salts, and that sulphuric is much less volatile than either nitric or hydrochloric acid. It is for this reason that sulphuric acid is also finally expelled from its salts when they are heated with much weaker, not volatile, acids, such as phosphoric or silicic. A few of the more important acids can be written in the following order, judging their strength by means of the relative amounts of metal which they will take from a chloride, when mixed with the latter in equivalent quantities:

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*Ostwald, Outlines of General Chemistry, p. 337 and sub.

1. Hydrochloric acid.
2. Nitric acid.
3. Hydrobromic acid.
4. Hydroiodic acid.
5. Sulphuric acid.
6. Selenic acid.
7. Phosphoric acid.
8. Hydrofluoric acid.
9. Silicic acid.

The heat produced by neutralizing an acid with a base has apparently nothing to do with the strength of this acid, for the greatest heat is produced by neutralizing hydrofluoric acid, and the next greatest with sulphuric acid, so that if were to take the relative heats of neutralization as indicating the relative strength of acids, quite a different order from the one given above would result, and certainly those salts which give the greatest amount of heat in their formation would in the dry state require the most energy for their decomposition. At some future time the relation between the heats of neutralization and the strength of an acid will undoubtedly be discovered.

CHAPTER XXII.

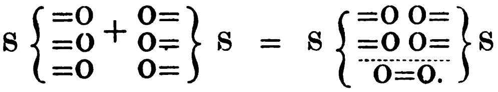
SULPHUR TRIOXIDE, SULPHURIC ACID AND THE REMAINING SULPHUR ACIDS.

Sulphur dioxide does not unite with oxygen under ordinary circumstances, but when a mixture of the two gases is passed over heated platinized asbestos, union takes place and sulphur trioxide is formed. When the latter is required for use in any quantity it is better to heat fuming sulphuric acid, as this substance contains a large quantity of the trioxide dissolved, or to heat an easily decomposed sulphate which will form a base and sulphur trioxide. Ferric sulphate is best for this purpose; the reaction takes place as follows:

$$Fe_2 (SO_4)_3 = Fe_2 O_3 + 3 SO_3.$$

The action of ozone on sulphur dioxide also produces the trioxide (pages 134 and 135).

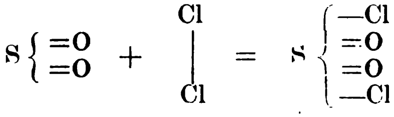
Pure sulphur trioxide is a colorless liquid at ordinary temperatures, but when gradually cooled it forms colorless prismatic crystals which melt at 15°. The substance boils at 46°, and forms a colorless vapor which has a specific gravity of 2.76, air being one, and therefore, hydrogen being two, of 79.48, its molecular weight is consequently 80 and the formula SO_3. The ordinary sulphur trioxide of commerce is a substance crystallizing in felt-like crystals resembling asbestos, and this form has been taken for a second modification of the body; in all probability, however, this difference in appearance is due to the presence of traces of water. Pure sulphuric anhydride does not redden litmus paper nor does it attack the hands, the acid and corrosive properties only appear when, by the addition of water, the substance is converted into sulphuric acid. Sulphur trioxide greedily absorbs moisture from the atmosphere; when a little of the substance is placed in water it unites with the latter with a hissing noise, like that produced in immersing a red hot iron. When heated to a red heat sulphur trioxide is dissociated, forming sulphur dioxide and oxygen; two volumes of sulphur trioxide yielding two volumes of SO_2 and one of O_2:



$$S\left\{\begin{matrix}=O\\=O\\=O\end{matrix}\right. + \left.\begin{matrix}O=\\O=\\O=\end{matrix}\right\}S = S\left\{\begin{matrix}=O\ O=\\=O\ O=\\O=O.\end{matrix}\right\}S$$

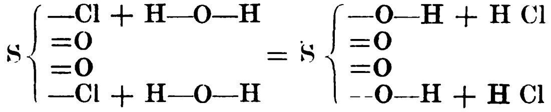
Sulphur trioxide is the anhydride of sulphuric acid and yields the latter on addition of water; $SO_3 + H_2O = H_2SO_4$.

The constitution of sulphuric acid will best be understood if we consider it as formed from sulphuryl chloride, SO_2Cl_2. We have seen that sulphur dioxide and chlorine unite to form sulphuryl chloride (page 135.) This change can be represented by structural formulæ as follows:



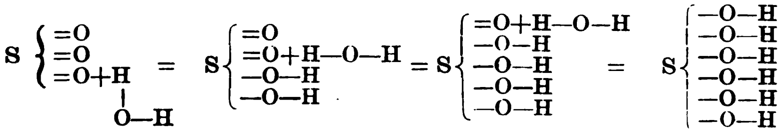
$$S\left\{\begin{matrix}=O\\=O\end{matrix}\right. + \begin{matrix}Cl\\|\\Cl\end{matrix} = S\left\{\begin{matrix}-Cl\\=O\\=O\\-Cl\end{matrix}\right.$$

Now, sulphuryl chloride, when water is added, breaks down into sulphuric acid and hydrochloric acid, and it is obvious that in such a reaction the chlorine atoms must be replaced by hydroxyle groups, so that sulphuric acid must contain two of the latter. The following formulæ will make this conclusion apparent:



$$S\left\{\begin{matrix}-Cl + H-O-H\\=O\\=O\\-Cl + H-O-H\end{matrix}\right. = S\left\{\begin{matrix}-O-H + H\,Cl\\=O\\=O\\-O-H + H\,Cl\end{matrix}\right.$$

Sulphuric acid can successively take up one and two molecules of water to form two hydrated acids, H_4SO_5, $(H_2SO_4 + H_2O)$ and H_6SO_6 $(H_2SO_4 + 2\,H_2O)$; it is in the latter form that the acid probably exists when a large excess of water is present, so that the three oxygen atoms of sulphuric anhydride, when the latter is dissolved, finally give place to six hydroxyle groups:



$$S\left\{\begin{matrix}=O\\=O\\=O+H\\\ \ \ \ |\\\ \ \ \ O-H\end{matrix}\right. = S\left\{\begin{matrix}=O\\=O+H-O-H\\-O-H\\-O-H\end{matrix}\right. = S\left\{\begin{matrix}=O+H-O-H\\-O-H\\-O-H\\-O-H\\-O-H\end{matrix}\right. = S\left\{\begin{matrix}-O-H\\-O-H\\-O-H\\-O-H\\-O-H\\-O-H\end{matrix}\right.$$

$$SO_3 + H_2O = H_2SO_4 + H_2O = H_4SO_5 + H_2O = H_6SO_6.$$

The two acids, $H_2SO_4 + H_2O$, and $H_2SO_4 + 2\,H_2O$, are known, but by far the greater number of sulphates are derived from H_2SO_4.

Sulphuric acid is one of the most important commercial products known, for the part which it plays in modern civilization is fundamental. We have but to consider that it is essential for the manufacture of soda, while soda is required to produce both soap and glass, in order to see that, if we can measure the civilization of a nation by the amount of soap which it uses, the quantity of sulphuric acid consumed can with greater reason be taken as an indication of the stage of development arrived at by a people.

The acid has been known since the time of the Arabian alchemists but was first accurately described by Basil Valentine, who prepared it in the fifteenth century by heating green vitriol (ferrous sulphate, Fe SO_4) with sand. The French emigrants of the reign of Louis XIV taught the English how to prepare the acid by oxidizing sulphur with nitre, and a quack doctor named Ward, using this method established, the first sulphuric acid factory in England, at Richmond. Dr. Ward partially filled a glass vessel of about 200 liters capacity with water, and then placed within this an earthen pot containing an iron ladle, on which was burning a mixture of sulphur and saltpetre, keeping the whole tightly covered until the combustion was complete. Of course this was all very crude, and the product proportionally dear, but nevertheless it was a vast improvement on the old alchemistic method, for the price of sulphuric acid was reduced from about three dollars and twenty-five cents to sixty cents a pound. In 1746 the glass vessel was replaced by a lead chamber and after this improvement exportation to the continent began, so that the acid became known as English sulphuric acid, a name which it bears to the present day. The next improvement consisted in substituting steam for water and in burning the mixture of saltpeter

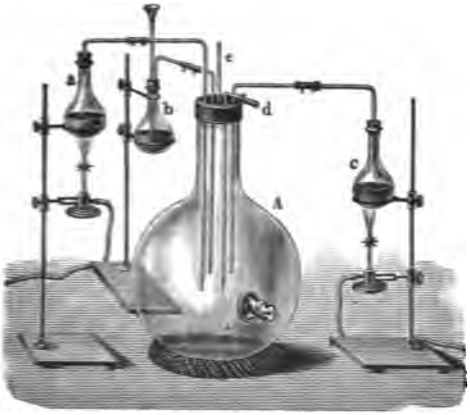


FIGURE 31.

and sulphur outside the chamber, while the water vapor was passed through a flue together with the products of oxidation, the process by this means becoming continuous. Finally the sulphur was burned in a separate furnace, while the sulphur dioxide so formed was oxidized in the chamber by means of nitric acid, and so the present continuous process evoluted from Dr. Ward's glass vessel, while the price of the acid sank from sixty cents to less than three cents a pound.

The manufacture of sulphuric acid is based upon the following changes:

$$SO_2 + H_2O = H_2SO_3,$$
$$H_2SO_3 + O = H_2SO_4,$$

and therefore its cheapness depends upon the ease with which sulphur dioxide can be prepared and upon the substance used as an oxidizer. It might not be unreasonable to suppose that the oxygen of the atmosphere would be most available for the purpose, but, unfortunately, sulphurous acid is oxidized much too slowly for commercial purposes by oxygen alone. If, however, we could furnish some ready means of conveying oxygen from the atmosphere to the sulphurous acid by the intervention of some chemical compound, the problem would be solved. This is done by means of nitric acid in the present continuous process; the main changes taking place in which are as follows:

1. A mixture of nitric acid and sulphurous acid act on each other, the sulphurous acid is *oxidized* to sulphuric acid and the nitric acid is *reduced* to nitrous acid.

$$2\,H_2SO_3 + 2\,HNO_3 = 2\,H_2SO_4 + 2\,HNO_2.$$

Nitrous acid, like other acids the anhydrides of which are gases, at once breaks down into water and nitrous anhydride:

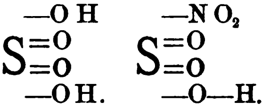
$$2\,HNO_2 = H_2O + N_2O_3,$$

so that the entire change can be represented by the equation:

$$2\,H_2SO_3 + 2\,HNO_3 = 2\,H_2SO_4 + H_2O + N_2O_3.$$

2. N_2O_3 with water, sulphur dioxide and oxygen forms a compound known as nitrosyl sulphuric acid, which latter is simply sul-

phuric acid in which an hydroxyle group is substituted by the group of elements NO_2*



$$\begin{array}{l} \quad -OH \\ S\begin{matrix}=O\\=O\end{matrix} \\ \quad -OH. \end{array} \qquad \begin{array}{l} \quad -NO_2 \\ S\begin{matrix}=O\\=O\end{matrix} \\ \quad -O-H. \end{array}$$

Sulphuric acid. Nitrosyl-sulphuric acid.

The reaction can be represented as follows:

$$2\,SO_2 + N_2O_3 + 2\,O + H_2O = 2\left\{\begin{array}{l} -OH \\ SO_2 \\ -NO_2. \end{array}\right.$$

3. Nitrosyl sulphuric acid breaks down into N_2O_3 and sulphuric acid on addition of water:

$$a.\quad S\left\{\begin{array}{l} OH \\ O_2 \\ \boxed{NO_2 + H}\ OH \end{array}\right. = S\left\{\begin{array}{l} OH \\ O_2 \\ OH \end{array}\right. + NO_2H,$$

b. $2\,NO_2H = N_2O_3 + H_2O$ so that combining a and b, we have

$$c.\ 2\,S\left\{\begin{array}{l} OH \\ O_2 \\ NO_2 \end{array}\right. + H_2O = 2\,H_2SO_4 + N_2O_3.$$

4. N_2O_3 is now regenerated, and with steam and air can once more form nitrosyl sulphuric acid which, with water, will form sulphuric acid, so that theoretically an infinitely small quantity of nitric acid introduced at the beginning of the operation would oxidize any amount of sulphur dioxide. That this is not the case in reality is due to the fact that other minor reactions, producing lower oxides of nitrogen, take place and also because the nitrogen of the air, as it takes no part in the reaction, gradually dilutes the gases to such an extent as to render loss inevitable. The commercial production of sulphuric acid is carried on in works of which a diagram is shown in Fig, 32." Sulphur dioxide is prepared by burning either sulphur or iron pyrites (FeS_2) in a furnace with free access of air; the gas enters the flue (*a*) and is conducted to the top of the tower (G) which is filled with pieces of fire brick. Two vats, (*b*), one containing dilute sulphuric acid and the other a concentrated acid in which oxides of

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* The group NO_2 is called the nitro group just as —O—H is called the hydroxyle group. It is univalent.

nitrogen are dissolved, are constantly emptying their contents into G. The latter acid is supplied from the tower G′, the object of which we shall see later on. Concentrated sulphuric acid can dissolve large quantities of the oxides of nitrogen, but dilute acid has no such power, so that mixing the contents of the two receptacles at (*b*) liberates these oxygen compounds. The acid and the oxides of nitrogen mingle with the sulphur dioxide entering at *a*; the hot gas serves to concentrate the dilute acid, while this cools the gas before it passes into the leaden chambers. Sulphur dioxide mixed with oxides of nitrogen, now enters the bottom of chamber 1, and, in this, comes in contact with steam and the vapors of nitric acid; the latter prepared by heating a mixture of sulphuric acid and sodium nitrate, by means of the sulphur burning to form sulphur dioxide. Sulphuric acid is formed in the first lead chamber, while the unused gases are passed into 2, and then into 3, in both of which places they come in contact with more steam, so that in these the changes are completed. The air, which is supplied by the draught of a large chimney, gives up its oxygen in going through the chambers, and therefore the gases become so diluted with nitrogen as to be no longer capable of taking part in the reactions. These diluted portions are passed in at the top of the tower G′, containing pieces of coke over which concentrated sulphuric acid is constantly trickling; here the acid dissolves the remaining oxides of

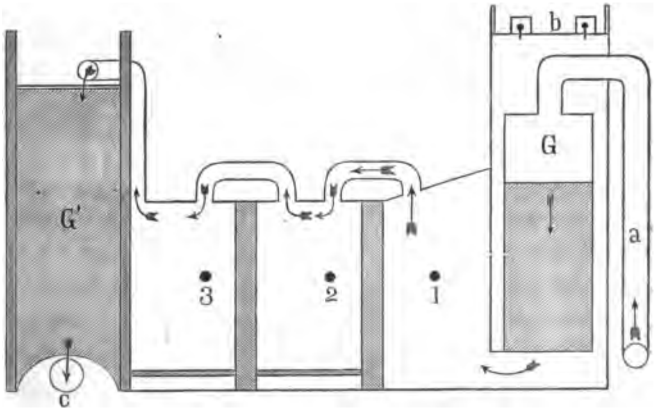

FIGURE 32.

nitrogen which pass from chamber 3, and, saturated with these gases, can be pumped to one of the vats *b* above the first tower, to be used as was indicated above. Experience has shown that the acid collected on the floors of the chambers must not contain more than 65–66 per cent. of H_2SO_4, and must not have a specific gravity higher than 1.5, but as the commercial acid has a specific gravity of 1.83 and must contain 89–90 per cent. of H_2SO_4, the concentration of the chamber acid is carried farther by placing it in flat lead pans and evaporating the excess of water until a specific gravity of 1.75 is reached, and then, because a stronger acid attacks lead, by finally completing the evaporation in platinum or glass vessels.

Commercial sulphuric acid is an oily liquid*, colored slightly brown by impurities. These consist of sulphate of lead, which is introduced from the lead chambers and which is never absent; of the oxides of nitrogen (N_2O_3 and NO_2); of hydrochloric acid and of arsenious oxide (As_2O_3), the latter because arsenic is found in the minerals roasted for the preparation of sulphur dioxide. In burning iron pyrites, the iron is changed to oxide and the sulphur to dioxide and, as the pyrites frequently contains selenium, selenium dioxide and selenium collect in the flues and in the muddy residue at the bottom of the chambers. The brownish color of commercial sulphuric acid is caused by organic substances which have fallen into it. Pure sulphuric acid is prepared from the commercial article by distilling from platinum vessels. Many so-called pure acids, however, contain arsenic, because arsenious oxide is volatile and will therefore pass over in the distillation, unless care has been taken to previously oxidize it to arsenic acid.

The pure acid, H_2SO_4, is a colorless oily liquid with a specific gravity of 1.85 at 0°. Upon being cooled to 0° it crystallizes in large prismatic crystals which melt at 10.5°, it boils at 338° but, before that temperature is reached it begins to decompose into sulphur trioxide and water, while, if the acid is heated somewhat above its boiling point, this separation is perfect:

$$H_2SO_4 = SO_3 + H_2O.$$

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*The name "oil of vitriol" was given to sulphuric acid by the alchemists because of its oily appearance and because it was first prepared from green vitriol (ferrous sulphate).

Sulphuric acid has a great inclination to take up water, and in so doing can form two hydrated acids: $H_4 SO_5$ and $H_6 SO_6$. The first one of these is formed when a mixture of $H_2 SO_4$, with just enough water, is cooled to a low temperature, then prisms of $H_4 SO_5$ separate. The second, or normal hydrate is produced by adding the requisite quantity of water to $H_4 SO_5$. A large amount of heat is developed in the formation of these hydrates, yet the heat production does not cease when exactly enough water to produce the normal hydrate has been added, it will continue until the proportions are expressed by $H_2 SO_4 + 1600\ H_2 O$, when 178 K will have been developed. Sulphuric acid has such a strong tendency to unite with water that it can take the elements of that compound from organic substances. If it is mixed with sugar, starch, pieces of wood, or similar substances which contain hydrogen and oxygen in exactly the proportions to form water, it will char them as if they had been burned, for, after the hydrogen and oxygen has been taken from such bodies, nothing but carbon remains. In a similar way sulphuric acid will attack the skin or mucous membrane, so that the concentrated acid is a violent poison.

Reducing agents readily change sulphuric acid to sulphur dioxide and even to sulphur, or sulphuretted hydrogen. We have studied examples of such reduction in the changes which took place when hydroiodic or hydrobromic acid acted upon sulphuric acid (see pages 71 and 81). As a general rule, hydrogen compounds will readily reduce sulphuric acid if, like hydroiodic and hydrobromic acids, they are unstable; for instance, hydrogen sulphide, selenide, or telluride will act in the following way:

$$H_2 SO_4 + H_2 S = 2\ H_2 O + SO_2 + S$$

This reaction is exactly like that taking place between hydrobromic and sulphuric acids:

$$H_2 SO_4 + 2\ H\ Br = 2\ H_2 O + SO_2 + 2\ Br,$$

only in the one case sulphur, and in the other bromine, is produced.

We have already discussed the reduction of concentrated sulphuric acid by metals (page 133), so that in this place it is only necessary to add that in addition to copper or zinc; silver, mercury, and a number of others will produce sulphur dioxide when heated with sulphuric acid, but we must remember that in cases where metals are attacked by the dilute acid, hydrogen is liberated, as we saw when we discussed the preparation of that element (see page 30). Other easily oxidized substances, like charcoal and sulphur, will also readily reduce sulphuric acid.

One of the chief laboratory uses of sulphuric acid is to prepare other acids by its action on the salts of the latter, and we have already encountered a number of cases in which it was applied for this purpose, for example:

$$\begin{aligned} 2\,\mathrm{K\,NO_3} &+ \mathrm{H_2\,SO_4} = \mathrm{K_2\,SO_4} + 2\,\mathrm{H\,NO_3},\\ 2\,\mathrm{K\,Cl\,O_4} &+ \mathrm{H_2\,SO_4} = \mathrm{K_2\,SO_4} + 2\,\mathrm{H\,Cl\,O_4}.\\ \mathrm{Na_2\,SO_3} &+ \mathrm{H_2\,SO_4} = \mathrm{Na_2\,SO_4} + \mathrm{H_2\,SO_3}.\\ 2\,\mathrm{Na\,Cl} &+ \mathrm{H_2\,SO_4} = \mathrm{Na_2\,SO_4} + 2\,\mathrm{H\,Cl}. \end{aligned}$$

Heretofore, in studying such relations, we have always taken the formation of the secondary sulphate for granted, but this in reality does not take place if an excess of sulphuric acid is present. Sulphuric acid is dibasic and we therefore can have two series of salts, the primary $\mathrm{MH\,SO_4}$ and the secondary $\mathrm{M_2\,SO_4}$. Now, if we compare the action of sulphuric acid on sodium nitrate or sodium chloride with that of the same acid on sodium hydroxide, we will see that they are analogous processes, and if we can, in acting on sulphuric acid with sodium hydroxide, replace first one and then both hydrogen atoms with the metal, it follows that we would have the same changes were we to substitute sodium chloride or sodium nitrate.

1. $$\mathrm{Na\,OH} + \begin{matrix}\mathrm{H{-}O}\\ \mathrm{H{-}O}\end{matrix} > \mathrm{S}\left\{\begin{matrix}=\mathrm{O}\\ =\mathrm{O}\end{matrix}\right. = \mathrm{H_2\,O} + \begin{matrix}\mathrm{Na\,{-}O}\\ \mathrm{H\ \ {-}O}\end{matrix} > \mathrm{S}\left\{\begin{matrix}=\mathrm{O}\\ =\mathrm{O}\end{matrix}\right.$$

$$\mathrm{Na\,OH} + \mathrm{H_2\,SO_4} = \mathrm{H_2\,O} + \mathrm{Na\,H\,SO_4}$$

2. $$\begin{matrix} & \mathrm{Na\,{-}O}\\ \mathrm{Na\,OH} + & \mathrm{H{-}O}\end{matrix} > \mathrm{S}\left\{\begin{matrix}=\mathrm{O}\\ =\mathrm{O}\end{matrix}\right. = \mathrm{H_2\,O} + \begin{matrix}\mathrm{Na\,{-}O}\\ \mathrm{Na\,{-}O}\end{matrix} > \mathrm{S}\left\{\begin{matrix}=\mathrm{O}\\ =\mathrm{O}\end{matrix}\right.$$

$$\mathrm{Na\,OH} + \mathrm{Na\,HSO_4} = \mathrm{H_2\,O} + \mathrm{Na_2\,SO_4}$$

1. $$\mathrm{Na\,Cl} + \begin{matrix}\mathrm{H{-}O}\\ \mathrm{H{-}O}\end{matrix} > \mathrm{S}\left\{\begin{matrix}=\mathrm{O}\\ =\mathrm{O}\end{matrix}\right. = \mathrm{H\,Cl} + \begin{matrix}\mathrm{Na\,{-}O}\\ \mathrm{H\ \ {-}O}\end{matrix} > \mathrm{S}\left\{\begin{matrix}=\mathrm{O}\\ =\mathrm{O}\end{matrix}\right.$$

$$\mathrm{Na\,Cl} + \mathrm{H_2\,SO_4} = \mathrm{H\,Cl} + \mathrm{Na\,HSO_4}$$

2. $$\begin{matrix} & \mathrm{Na{-}O}\\ \mathrm{Na\,Cl} + & \mathrm{H{-}O}\end{matrix} > \mathrm{S}\left\{\begin{matrix}\ \ \mathrm{O}\\ =\mathrm{O}\end{matrix}\right. = \mathrm{H\,Cl} + \begin{matrix}\mathrm{Na\,{-}O}\\ \mathrm{Na\,{-}O}\end{matrix} > \mathrm{S}\left\{\begin{matrix}=\mathrm{O}\\ =\mathrm{O}\end{matrix}\right.$$

$$\mathrm{Na\,Cl} + \mathrm{Na\,HSO_4} \qquad \mathrm{H\,Cl} + \mathrm{Na_2\,SO_4}.$$

The above reactions are a necessary result of the fact that in polybasic acids the hydrogen atoms are intirely independent of each other. If, therefore, in decomposing a salt, we use an excess of sulphuric acid, the primary sulphate results, if we use an excess of the salt, we produce the secondary sulphate, for comparing the two reactions;

$NaCl + H_2SO_4 = NaHSO_4 + HCl$, and $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$,

we see that in the second one we have *twice* as much sodium chloride in proportion to the acid as in the first. In laboratory practice it is expedient to so calculate the relative quantities of salt and sulphuric acid as to always produce the primary sulphate, because the latter is easier to fuse and more convenient to handle than the secondary. On heating a primary sulphate* we form the corresponding secondary sulphate thus:

$$2\,NaHSO_4 = Na_2SO_4 + H_2SO_4$$

and we can accomplish the same result by adding a base;

$$NaHSO_4 + NaOH = Na_2SO_4 + H_2O,$$

but it is obvious that the hydroxide so added may contain a different metal from that already present in the salt, so that secondary salts containing two metals may be formed;

$$NaHSO_4 + KOH = NaKSO_4 + H_2O.$$

By adding sulphuric acid to the secondary sulphate we can produce the primary one:

$$Na_2SO_4 + H_2SO_4 = 2\,NaHSO_4.$$

No salts formed by replacing all of the hydrogen atoms in either of the other two hydrated acids, H_4SO_5 and H_6SO_6, exist, but some are known in which a metal has been substituted for two of these; such salts are frequently considered as being ordinary sulphates with the additional water attached in some mysterious way known as "molecular union" and so their formulæ are written $MSO_4 + H_2O$ and $MSO_4 + 2\,H_2O$, but it is more rational to look upon these as secondary salts MH_2SO_5 and MH_4SO_6 of the hydrated acids, H_4SO_5 and H_6SO_6. This theory is born out by the fact that many of these salts only lose water at temperatures considerably above that necessary to expel water of crystallization, which fact seems to indicate that water, as such, is not present in them, but that it is in the form of hydroxyle. A number of more complicated salts are supposed to be derived from normal sulphuric acid, but for information regarding these a larger manual must be consulted.

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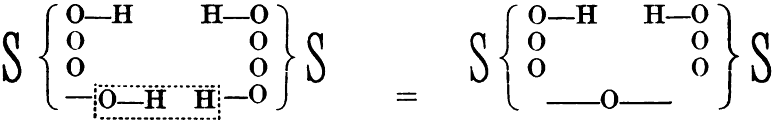
* Also termed an acid or a bisulphate.

Sulphur trioxide is very soluble in sulphuric acid, forming an oily liquid which gives off dense white fumes in the air:

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

This solution, which has the composition $H_2S_2O_7$, is known as fuming sulphuric acid; it is derived from sulphuric acid by separating water from hydroxyle groups belonging to separate molecules. so that its constitution would be represented as follows:



$$S\left\{\begin{array}{llll} O—H & & & H—O \\ O & & & O \\ O & & & O \\ — & \boxed{O—H \quad H} & & —O \end{array}\right\}S = S\left\{\begin{array}{lll} O—H & & H—O \\ O & & O \\ O & & O \\ & —O— & \end{array}\right\}S$$

This acid is therefore a dibasic acid, formed by linking two monovalent groups SO_3H by means of a divalent oxygen atom, and its name, disulphuric acid, suggests this constitution. The union of two such monovalent groups by means of a polyvalent atom is a phenomenon of quite common occurrence. On adding water to disulphuric acid, sulphuric acid is formed and on extracting water from disulphuric acid, sulphur trioxide remains, so that this acid lies between sulphuric acid and its anhydride, bearing the same relationship to sulphuric acid as the latter does to H_4SO_5:

$$H_2S_2O_7 + H_2O = 2\,H_2SO_4,$$
$$H_2S_2O_7 — H_2O = 2\,SO_3.$$

We have seen that, because of the great chemical similarity between the two elements, sulphur can take the place of oxygen in acids. We are acquainted with the salts of one acid (thiosulphuric acid), derived from sulphuric acid in which such a substitution has taken place; the acid itself is not known. Thiosulphate of sodium $Na_2S_2O_3$, the most common salt of this acid, can be considered as sulphate of sodium in which one atom of oxygen has been replaced by one of sulphur:

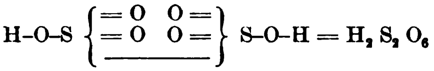
Na_2SO_4, sodium sulphate and Na_2SSO_3 sodium thiosulphate.

This compound is frequently called the hyposulphite of sodium, but obviously such a name is not advisable because it suggests a relationship to sulphurous acid similar to that sustained by hypochlorous acid to chlorous acid, while such a parallelism does not in reality exist. The thiosulphate is changed to the sulphate by heating, all of the oxygen being used to form the latter salt, while the excess of sulphur unites with the excess of metal to form the sulphide.* When thiosulphuric acid is liberated from its salts by the addition of other acids it at once breaks down into water, sulphur dioxide and sulphur.

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2 + S.$$

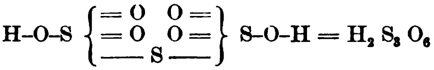
In addition to those which have been mentioned, a series of acids containing sulphur and which have the following formulæ exists:

1. Dithionic acid,



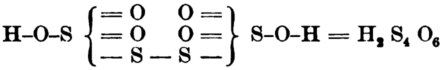
$$\mathrm{H{-}O{-}S}\left\{\begin{array}{c} =\mathrm{O}\quad\mathrm{O}= \\ =\mathrm{O}\quad\mathrm{O}= \\ \hline \end{array}\right\}\mathrm{S{-}O{-}H} = H_2S_2O_6$$

2. Trithionic acid,



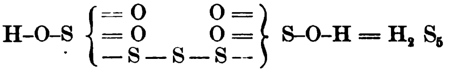
$$\mathrm{H{-}O{-}S}\left\{\begin{array}{c} =\mathrm{O}\quad\mathrm{O}= \\ =\mathrm{O}\quad\mathrm{O}= \\ \text{——S——} \end{array}\right\}\mathrm{S{-}O{-}H} = H_2S_3O_6$$

3. Tetrathionic acid,



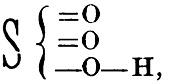
$$\mathrm{H{-}O{-}S}\left\{\begin{array}{c} =\mathrm{O}\qquad\mathrm{O}= \\ =\mathrm{O}\qquad\mathrm{O}= \\ -\mathrm{S}-\mathrm{S}- \end{array}\right\}\mathrm{S{-}O{-}H} = H_2S_4O_6$$

4. Pentathionic acid,



$$\mathrm{H{-}O{-}S}\left\{\begin{array}{c} =\mathrm{O}\qquad\quad\mathrm{O}= \\ =\mathrm{O}\qquad\quad\mathrm{O}= \\ -\mathrm{S}-\mathrm{S}-\mathrm{S}- \end{array}\right\}\mathrm{S{-}O{-}H} = H_2S_5O_6.$$

They can all be considered as containing the univalent group of elements,



$$\mathrm{S}\left\{\begin{array}{l} =\mathrm{O} \\ =\mathrm{O} \\ -\mathrm{O}-\mathrm{H}, \end{array}\right.$$

which occurred in disulphuric acid (see page 150). Two of these are united in dithionic acid, while in the remaining three they are joined by means of sulphur atoms, as is shown by the formulæ. Trithionic acid therefore is disulphuric acid in which the linking oxygen atom is replaced by one of sulphur. A larger text-book must be consulted for the methods of preparation and general characteristics of these acids. The constitutional formulæ of the compounds which, in the course of our study, have followed sulphuric acid express the present state of our knowledge, but the whole subject will bear further investigation. Constitutional formulæ are constructed because the peculiar arrangements of atoms in them seem to be the ones which explains all of the reactions entered into by the substances which they represent and which are also indicated by the manner in which these substances are formed.

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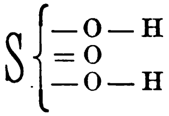
*The formulæ of the sulphides of some metals, notably those of the alkali metals, certainly bear a most remarkable resemblance to the oxygen compounds we have just been studying. Thus we have sulphides of potassium, K^2S^2, K^2S^3, K^2S^4 and K^2S^5, called polysulphides, the last two of which when written K^2SS^3 and K^2SS^4 might possibly be K^2SO^3 and K^2SO^4 in which oxygen is replaced by sulphur; as, however, the parallelism does not extend beyond the mere relationship in the number of atoms, and as we have no knowledge of the structural formulæ of the polysulphides, this interpretation is purely speculative.

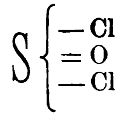
As might be expected, sulphur can form unstable chlorides by direct union with chlorine. The first product of the action of chlorine on sulphur is the monochloride, $S_2 Cl_2$, if the action of chlorine is continued the dichloride, $S Cl_2$, is formed, and lastly if a large excess of chlorine acts on the dichloride at a temperature of —22° the tetrachloride, $S Cl_4$, results. This latter compound decomposes when warmed above —22°, while the dichloride is only stable below 6 to 10°. Corresponding compounds, $S_2 Br_2$ and $S_2 I_2$, exist.

Compounds of sulphur containing both chlorine and oxygen are formed from sulphurous and sulphuric acids, by substituting chlorine for hydroxyle groups. They are called acid chlorides and are $SO Cl_2$, thionyl chloride, $SO_3 Cl H$ sulphuryl-hydroxyl chloride and $SO_2 Cl_2$, sulphuryl chloride.



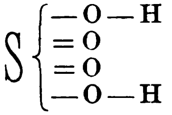
$$S\left\{\begin{array}{l}-O-H\\=O\\-O-H\end{array}\right.$$

Sulphurous acid.



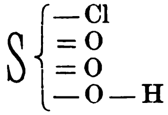
$$S\left\{\begin{array}{l}-Cl\\=O\\-Cl\end{array}\right.$$

Thionyl chloride.



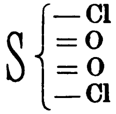
$$S\left\{\begin{array}{l}-O-H\\=O\\=O\\-O-H\end{array}\right.$$

Sulphuric acid.



$$S\left\{\begin{array}{l}-Cl\\=O\\=O\\-O-H\end{array}\right.$$

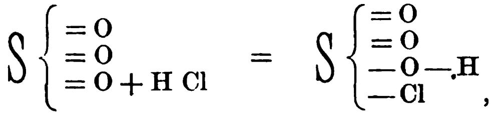
Sulphuryl-hydroxyl chloride.



$$S\left\{\begin{array}{l}-Cl\\=O\\=O\\-Cl\end{array}\right.$$

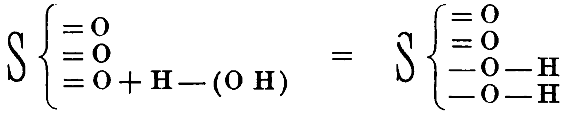
Sulphuryl chloride.

Following the law which we found to be general with the chlorides of the not-metals, these compounds are decomposed into the corresponding acids by addition of water; thionyl chloride forming sulphurous acid and the last two both yielding sulphuric acid. The decomposition of sulphuryl chloride in this way not only has an important theoretic bearing in the constitution of sulphuric acid, (See page 141) but what is more, the formation of $SO_3 Cl H$ from hydrochloric acid and sulphuric anhydride:

1. 

$$S\left\{\begin{array}{l}=O\\=O\\=O\end{array}\right. + H\,Cl \quad = \quad S\left\{\begin{array}{l}=O\\=O\\-O-H\\-Cl\end{array}\right.,$$

shows a resemblance between hydrochloric acid and water in chemical behavior; for the following reaction (2) is clearly analogous to reaction 1:

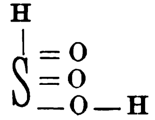
2. 

$$S\begin{cases}=O\\=O\\=O\end{cases}+H-(O\,H) = S\begin{cases}=O\\=O\\-O-H\\-O-H\end{cases}$$

The existence of these compounds illustrates the similarity of the hydroxides of the metals to those of the not-metals, for in both classes of compounds the hydroxyle groups can be replaced by chlorine; only with metals this substitution is much more easily brought about than with not-metals. The hydroxide of the metal has only to be treated with hydrochloric acid in order to form the very stable chloride:

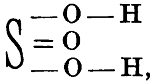
$$K-O-H+H\,Cl=K\,Cl+H-O-H,$$

while in forming the acid chlorides some roundabout method, which excludes the presence of water, must be resorted to, for these compounds are decomposed by the latter substance. Chemists have lately looked upon sulphurous acid as being:

I. 

$$\begin{array}{l}H\\|\\S\begin{array}{l}=O\\=O\\-O-H\end{array}\end{array}$$

and not as

II. 

$$S\begin{array}{l}-O-H\\=O\\-O-H,\end{array}$$

so that an analogy between that acid and thionyl chloride would not exist. This interpretation, which they have given to some experiments made with organic compounds, seems to be unnecessary, it is more probable that the replaceable hydrogen in all of these acids which we have studied, and which contain oxygen, is present in the hydroxyle groups, so that the formula of sulphurous acid would be as is shown above. (II.)

Two other oxides of sulphur, $S_2\,O_3$ and $S_2\,O_7$, are known. Both of these very readily decompose, the former into sulphur and sulphur dioxide, ($S_2\,O_3 = S + SO_2$) and the latter into sulphur trioxide and oxygen ($S_2\,O_7 = 2\,SO_3 + O$).

The following table will make the relationship between the sulphur acids more apparent.

$SO_2 + 2\,Cl = SO_2Cl_2$.

The compounds $\underbrace{SOCl_2 \qquad SO_2}$ .... and ....$\underbrace{SO_2Cl_2 \qquad SO_3}$

with water yield H_2SO_3 .... and .... H_2SO_4

Sulphurous acid. Sulphuric acid.

H_2SO_4
$+SO_3$
$H_2S_2O_7$
Disulphuric acid.

$H_2SO_3 + O =$ .... H_2SO_4.................... $-H_2O$

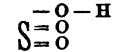
SO_3
Sulphuric anhydride.

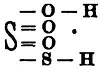
H_2SO_4
$+H_2O$
H_4SO_5
$+H_2O$
H_6SO_6
Normal sulphuric acid.

$MHSO_3 + MOH$	-	$M_2SO_3 + H_2O$.
Primary sulphite.		Secondary sulphite.
$M_2SO_3 + H_2SO_3$	=	$2\,MHSO_3$.
Secondary sulphite.		Primary sulphite.
$MHSO_4 + MOH$	=	$M_2SO_4 + H_2O$.
Primary sulphate.		Secondary sulphate.
$M_2SO_4 + H_2SO_4$	=	$2\,MHSO_4$.
Secondary sulphate.		Primary sulphate.

Heating the primary sulphate produces the secondary sulphate and sulphuric acid.

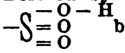
Heating the primary sulphite produces the secondary sulphite and sulphurous acid.


$$S\begin{cases}-O-H\\=O\\=O\\-O-H\end{cases}$$
Sulphuric acid.


$$S\begin{cases}-O-H\\=O\\=O\\-S-H\end{cases}$$
Thiosulphuric acid.

$Na_2S_2O_6$ Dithionic acid.
$Na_2S_3O_6$ Trithionic acid.
$Na_2S_4O_6$ Tetrathionic acid.
$Na_2S_5O_6$ Pentathionic acid.

Derived by uniting the univalent group


$$-S\begin{cases}-O-H\\=O\\=O\end{cases}$$

by means of sulphur atoms.

CHAPTER XXIII.

THE COMPOUNDS OF SELENIUM AND TELLURIUM WITH OXYGEN AND WITH OXYGEN AND HYDROGEN.

Selenium and tellurium do not manifest so great a variety in the formation of oxides and acids as does sulphur, but such oxides as they do form are constructed in an analogous manner. They each, on burning, yield the corresponding dioxide:

$$Se + 2\,O = Se\,O_2 \text{ and } Te + 2\,O = Te\,O_2$$

and both the dioxides are solid bodies, in fact all of the oxides of the not-metals with higher atomic weight are solids. Sulphur dioxide, in solution, is a powferful reducing agent, always showing the greatest tendency to take up oxgen so as to form sulphuric acid, while on the other hand the dioxides of selenium and tellurium exhibit a behavior which is exactly the reverse, they part with their oxygen so readily that even the particles of dust which may come in contact with them, serve to liberate selenium or tellurium. Of course, sulphurous acid readily reduces the two oxides, while it changes to sulphuric acid:

$$2\,H_2\,SO_3 + Se\,O_2 = 2\,H_2\,SO_4 + Se,$$
$$2\,H_2\,SO_3 + Te\,O_2 = 2\,H_2\,SO_4 + Te,$$

and as a consequence selenium and not selenium dioxide is found in the lead chambers of sulphuric acid works. (See page 97.)

Selenium dioxide is a white, snow-like solid, which is best prepared by oxidizing selenium with nitric acid. It does not melt, but on heating it changes directly from a solid to a gas at a temperature below the boiling point of sulphuric acid. Selenium dioxide greedily absorbs moisture from the air, forming selenious acid. The latter is a dibasic acid, giving primary and secondary salts, $MH\,Se\,O_3$ and $M_2\,Se\,O_3$.

Tellurium dioxide is also produced by the oxidation of tellurium with nitric acid. It is a colorless crystalline solid, but little soluble in water. As tellurium has such a high atomic weight, its lower oxides begin to bear some resemblance to those of the less pronounced metals; the dioxide has therefore scarcely any tendency to unite with water nor is it dissolved by weak bases; an additional sign that tellurium is approaching the metals in its character is the fact that the tetrachloride, $Te\,Cl_4$, is not completely decomposed by cold water. Tellurous acid is a white powder which readily decomposes into tellurium dioxide and water on warming. It is a dibasic acid and forms primary and secondary salts, $MH\,Te\,O_3$ and $M_2\,Te\,O_3$.

Selenium trioxide has never been prepared, but the corresponding acid, $H_2\,Se\,O_4$, selenic acid, can be formed by oxidizing selenious acid with chlorine or bromine, just as the corresponding sulphur compound was oxidized by the same elements. Solutions of selenic acid cannot be concentrated so that they contain more than 95 per cent. of $H_2\,Se\,O_4$, because, after that point is reached, the acid breaks down into selenious acid and oxygen; so that the rule with the selenium acids is exactly the reverse of that which held true as regards the halogene and the sulphur compounds, for in those, the acids containing the most oxygen were the final products formed by heating those containing the lesser. Selenic acid is dibasic and forms primary and secondary salts, $MH\,Se\,O_4$ and $M_2\,Se\,O_4$.

The properties of telluric acid are much like those of selenic acid with the exception that the anhydride $Te\,O_3$ is known. The latter compound is produced by heating telluric acid, which breaks down into its anydride and water, $H_2\,Te\,O_4 = Te\,O_3 + H_2\,O$. The oxygen compounds of the sulphur family are exactly parallel with those of the halogene family as regards stability. Thus fluorine could form no oxide, and the oxide of oxygen (ozone) is quite unstable; chlorine forms a greater variety of oxides than does any other element of the halogenes, while sulphur exhibits the same property in its own family. The third members of either family, selenium and bromine, are the elements which, next to the first member of each family, have the least tendency to form oxides, while with iodine and tellurium the capacity to form stable oxides is once more manifested.

Both selenium and tellurium can form compounds with sulphur, but while those of selenium, excepting the simplest (the monosulphide Se S,) are not very definitely understood, those of tellurium exactly correspond to the oxygen compounds of that element, so that we have a disulphide $Te\ S_2$ and a trisulphide $Te\ S_3$, and this latter compound resembles the trioxide $Te\ O_3$ so far as to be the anhydride of an acid, for with sulphides, like those of sodium or potassium, it will form salts in which all of the oxygen is replaced by sulphur:

$$K_2\,S + Te\,S_3 = K_2\,Te\,S_4$$
$$K_2\,O + Te\,O_3 = K_2\,Te\,O_4.$$

The existence of such a compound as $K_2\ Te\ S_4$ is another proof of the great resemblance between sulphur and oxygen.

The chlorine compounds of selenium and tellurium are like those of sulphur.

The following table contains the thermo-chemical relations which exist between the oxides of the sulphur family and between the acids $H\ XO_3$ of the halogene family. Unfortunately, the heats of formation of the oxides of the halogenes have not been accurately determined, so that in this table we are compelled to compare oxides with compounds of oxygen and hydrogen:

				Stability.
SO_2	710 K	$H\,Cl\,O_3$	239 K	∨
$Se\,O_2$	572 K	$H\,Br\,O_3$	160 K	
$Te\,O_2$	773 K	$HI\,O_3$	582 K	∧
Heats of formation of the chlorides.				Stability.
$S_2\,Cl_2$	143 K	——	——	∧
$Se_2\,Cl_2$	222 K	$Se\,Cl_4$	462 K	
——	——	$Te\,Cl_4$	774 K	

The heats of formation and stability of the chlorine compounds increase with the atomic weights, and therefore increase with the decreasing not-metallic character of the elements. This rule is reversed with the hydrogen compounds, so that in this family the chlorine and the hydrogen compounds are less easily decomposed, the greater the chemical contrast between the elements forming them.

CHAPTER XXIV.

NITROGEN AND THE ATMOSPHERE.

Nitrogen, Symbol N, atomic weight 14.03, specific gravity, air = 1 is .9713, H = 2 is 27.9, 1 c. c. at 0° and .76m weighs .00125 grams. The Atmosphere, specific gravity 1; 1 c. c. air at 0° and .76m pressure weighs .001299 grams.

As the atmosphere is simply a mixture of gases, with nothing in its deportment from which general chemical comparisons could be made, it seems advisable to treat of it in a separate chapter; subsequently introducing the characteristics which the elements of the nitrogen family have in common. A description of the element nitrogen must, however, be given before the atmosphere is considered.

An English chemist, Rutherford, noticed in 1772 that air in which an animal had breathed became unfit to further support either combustion or life, even after care had been taken to remove all of the carbon dioxide by means of lime water or caustic potash, and he therefore came to the conclusion that the residuum contained a peculiar kind of air. When subsequently it was discovered that elements which formed solid oxides, when burned in a closed space of air, left nothing but this same gas, the general consensus of opinion among chemists was that this latter must be phlogisticated air, for the burning substance had given up its phlogiston and that portion of the atmosphere which remained must as a consequence have taken it up, while oxygen, in which substances burned so readily, was therefore most certainly pure dephlogisticated air. These theories as regards the nature of the atmosphere were unfortunate for the older school of chemists, for it was not difficult to prove that carbon, in burning in oxygen, or as they said, in giving up its phlogiston, formed a different kind of phlogisticated air, which was likewise unable to support either life or combustion. Lastly, hydrogen, which was supposed to be pure phlogiston, when burned in dephlogisticated air formed water; therefore the latter should also be phlogistical air, yet it differed entirely from both of the other forms. As a consequence, chemists were brought face to face with the necessity of assuming the existence of three different kinds of phlogisticated air. It was left for Lavoisier to prove the fallacy involved in these theories and to show that the atmosphere contained two distinct gases, one of which he called oxygène, the other azote (from α and ζωτικὸς, to sustain life). The name nitrogène (from nitrum, saltpetre and the root γεν, to produce) was introduced by Chaptal, and from this the English name, nitrogen, has resulted, The word azote is still used by French chemists.

Nitrogen occurs as such, in the atmosphere and dissolved in small quantities in water; combined it is found in the form of sodium nitrate or Chili saltpetre, large deposits of which occur in the northern provinces of Chili, and as ammonium compounds which are found in small quantities in the air and in the soil; nitrogen is also an essential constituent of many organic substances of both animal and vegetable origin. Despite its wide distribution, nitrogen forms scarcely one per cent. of the total substance of the globe, even if we include in this its gaseous envelope, for very little, if any, nitrogen is found in the older geologic formations.

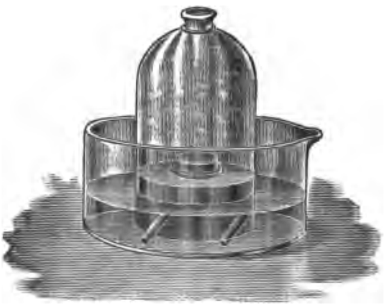


FIGURE 33.

While we are acquainted with no simple method by which to remove the nitrogen from the atmosphere so as to obtain the oxygen contained therein, the removal of the latter element is a comparatively simple matter; to do this it is only necessary to burn some substance in a closed volume of air; however, it is expedient to combust a body which will form a solid oxide and which will therefore leave no gaseous residuum excepting nitrogen. Phosphorus answers this purpose admirably, for when it is burned it forms phosphorus pentoxide, a solid readily soluble in water.[45] Another method for preparing nitrogen is by passing air over copper foil heated in an infusible glass tube by means of a combustion furnace; the copper then becomes oxidized, copper oxide, Cu O, being formed, while the unchanged nitrogen passes on, to be collected over water.

Nitrogen is a colorless, odorless gas, with a specific gravity, air being one, of .9713, and hydrogen being two, of 27.9, so that, as the atomic weight of the element is 14, the molecule of nitrogen consists of two atoms, just as was the case with oxygen, hydrogen and chlorine. Its critical temperature is —146.3° at a pressure of 35 atmospheres. This means that at —146.3° nitrogen becomes fluid if a pressure of 35 atmospheres is exerted, but that above this temperature pressure cannot condense it to a liquid. The boiling point of liquid nitrogen is at —193°, with a pressure of 740 m. m.; the freezing point is at —203°. Nitrogen is scarcely soluble in water, for one volume of the latter dissolves only .015 volumes of the gas at ordinary temperatures.

Chemically, nitrogen is a remarkably indifferent substance when in the free state, a circumstance which is very striking when we consider that the same element, when combined with others, can take part in a great number of chemical reactions, manifesting therein the greatest chemical activity. Nitrogen will unite with other elements only under the greatest provocation; so, for instance, nitrogen and hydrogen will form ammonia under the influence of an electric current, and nitrous acid, nitric acid and ammonium nitrate are formed in small quantities when hydrogen burns in air. Owing to its chemical indifference, nitrogen will neither burn nor support combustion, and, naturally, animals when placed in the gas die from asphyxia.

Toward the latter part of the eighteenth century, when chemists began to inquire into the nature of the atmosphere, the determination of the exact quantities of nitrogen and oxygen going to form that gas became an interesting subject for research. Lord Cavendish first made a series of accurate investigations of the air in and about London, coming to the conclusion that there were about 79 out of every 100 volumes of air left as phlogisticated air after combustion had taken place. Lavoisier, of course, also studied the subject, but with very uncertain results, for at one time he gave the volume of oxygen as one fourth, at another time as one fifth of the total atmosphere. Gay Lussac and Humboldt made some really accurate determinations of air in the neighborhood of Paris, and they found that there were between 20.9 and 21.2 volumes of oxygen in every 100 volumes of air, while at a later date a great number of chemists, notably Dumas, Regnault and Bunsen made a large series of accurate determinations, the results of which showed that the atmosphere contained 20.9 volumes of oxygen and 79.1 volumes of nitrogen in every 100 volumes, but that these quantities were subject to frequent, but very slight, variations. The following figures will show the extent of these differences.

Lyons, Berlin,	20.9	volumes	of	oxygen	in	100	volumes	of	air.
Algiers,	20.4	"	"	"	"	100	"	"	"
Calcutta,	20.3	"	"	"	"	100	"	"	"
Atlantic Ocean,	21.5	"	"	"	"	100	"	"	"

These variations, which are so great as to fall without the range of experimental error, indicate that the atmosphere is a mechanical mixture and not a chemical compound. Another proof of this conclusion can be obtained by examining the difference in the solubility of oxygen and nitrogen in water. A given volume of water will dissolve quite a little more of oxygen than it will of nitrogen, so that if we place some water, which has been exposed to the air, under the bell of an air pump and then exhaust, the bubbles of gas which pass from the liquid will be a mixture of oxygen and nitrogen containing more of the former element than does the air. The gas so formed can again be dissolved in water and once more exhausted, and if the operation is repeated often enough with the same volume, this will finally be almost pure oxygen. The oxygen and nitrogen of the air can therefore be separated by simple, not chemical means. The discovery that oxygen and nitrogen can be mixed to form air without a change either in the total volume or in the amount of heat contained in the two gases, forms a final argument against the conception of the atmosphere as a chemical compound.[46]

While oxygen and nitrogen form the bulk of the atmosphere, other substances are always present in minute quantities. The most important of these impurities are carbon dioxide, ammonium carbonate, nitrate and nitrite and water vapor, as well as solid particles of dust which are both organic and inorganic in their origin. Carbon dioxide, which is invariably found in the air, is as important to living organisms as oxygen itself and of far greater value than is the uncombined nitrogen, for the latest investigations show that the admixture of the latter does not make the air more adaptable for respiration, for animals can live as comfortably in pure oxygen as they do in air; on the other hand carbon dioxide is a plant food absolutely necessary for vegetable life. Carbon dioxide is being constantly added to the atmosphere from burning fuel, from volcanic craters and fissures, from decomposing organic substances and from the breathing of animals, because it is produced by the combustion or decay of carboniferous substances. If no means were provided for the removal of the atmospheric carbon dioxide, the increase in the amount of the latter would soon destroy all living organisms dependent upon respiration. Fortunately, plants growing in the sunlight absorb carbon dioxide from the air, by means of a green coloring matter which can eliminate oxygen from, and add hydrogen to, carbon dioxide, and which is contained in their leaves, so that a substance which is able to form all of the innumerable compounds of carbon, hydrogen and oxygen occurring in the vegetable kingdom, is produced by this means.[*]

The carbon dioxide of the atmosphere is therefore continually being removed while oxygen is being returned, but were this process to go on without any compensating production of carbon dioxide, plant life and consequently animal life would soon cease. The supply of carbon dioxide is however renewed by one means or another, so that the quantity in the atmosphere remains quite constant. In former geologic periods the atmosphere was undoubtedly much warmer and contained much greater quantities of carbon dioxide than it does now. Hot rains were continually pouring down and

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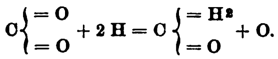
[*] According to the view held by many chemists, this substance is formic aldehyde, $CH^2 O$; or



$$C\left\{\begin{matrix} =O \\ \\ =O \end{matrix}\right. + 2H = C\left\{\begin{matrix} =H^2 \\ \\ =O \end{matrix}\right. + O.$$

This can be considered as carbon dioxide in which one atom of oxygen has been replaced by two of hydrogen; it therefore contains the elements hydrogen and oxygen in exactly the proportions necessary to form water, while sugars, starch and cellulose also contain the elements in the same proportions. Glucose has the formula $C^6 H^{12} O^6 = 6 (C H^2 O)$ so that it can very possibly be formed by simple condensation of six formic aldehyde molecules and, indeed, a substance very nearly identical with glucose has been made artificially by this means. Cane sugar, starch and cellulose are made from $C^6 H^{12} O^6$ by separation of water between the molecules, so that the theory of the reduction of carbon dioxide by plants to form formic aldehyde seems very reasonable. The hydrogen for this reduction is probably furnished by the decomposition of water, the oxygen of which is eliminated.

copiously watering the continents and islands which had been formed, so that vegetation on a gigantic scale flourished wherever the soil was favorable. Our coal beds were produced by the destruction of the flora of that period; by this means enormous quantities of carbon dioxide were removed from the atmosphere, and the carbon stored for use when the supply of that gas should no longer be sufficient to support vegetation. After the atmosphere had assumed the composition which it possesses at present, animal life flourished. The plants took up carbon dioxide from the atmosphere, formed their tissues therefrom, animals lived on them or preyed on each other; both plants and animals died, decayed, and the carbon dioxide once more found its way into the atmosphere; so that a continuous metamorphosis, with its energy given by the light and heat of the sun, was in progress. Small quantities of carbon dioxide were, however, lost in the formation of carbonates of the metals because, in disintegrating, the silicates, which mainly formed the rocks, liberated the bases which they contained, so that these could unite with other acids of which carbonic acid was one, and thus a certain amount of the latter substance was permanently removed from the atmosphere. This loss has been supplied by the carbon dioxide of volcanic origin and by that formed in burning the fuel which was stored as coal in a former geologic era, so that, as far as we know, the amount of carbon dioxide in the atmosphere is not diminishing; if it is growing less the rate of decrease is so very slow that in the short time during which chemists have been able to make accurate observations, no change could be noted. The amount of carbon dioxide in the air varies slightly, but normally it is about

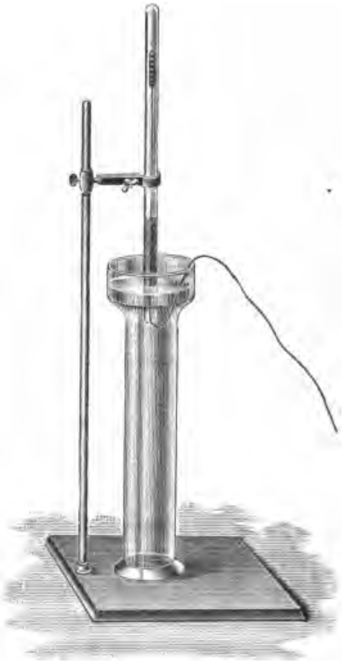


FIGURE 34.

four parts in ten thousand, and it seems that the amount of carbon dioxide is greater at night than in the day time, and in summer than in winter. In the higher regions of the atmosphere, where vegetation is impossible, the amount of the gas may even increase to eleven parts in ten thousand, while a continued rain storm may diminish it to two and a quarter. The amount of carbon dioxide in crowded rooms is increased by the breathing of the people within the closed air space, yet this does not generally take place to such an extent that the oppressive feeling caused by such an atmosphere can be ascribed entirely to it; the unpleasant effect is due to exhalations of an organic nature which pass from the lungs. The presence of carbon dioxide in the atmosphere can be proved at any time by exposing some clear lime water to the action of the latter, for a white crust of the carbonate of calcium will be formed in a short time.[47]

Water vapor is always present in the atmosphere in quantities varying with the temperature, season of the year and locality; it is just as important as carbon dioxide to living organisms. The evaporation of oceans, lakes and rivers furnishes a never ending supply of water, the amount of which is generally greater in hot than in cold weather, and greater by day than by night.

The higher the temperature of a gas the greater will be the amount of water vapor which it can take up, for the quantity of the latter which can be contained in a closed space (either a vacuum or filled with gas) increases with the temperature, but is an unalterable amount at any definite point. If as much water vapor as can possibly be present at the existing temperature is contained in a gas, the latter is said to be saturated and no further evaporation of water can take place unless the temperature is increased; on the other hand a decrease of the latter would diminish the amount of vapor which can be present, so that a portion of the moisture would be precipitated as water. From these considerations it follows that if the atmosphere is nearly saturated with moisture, any diminution in the temperature will cause a fall of rain or the formation of dew, while at the same time no evaporation can take place when such a condition prevails. The amount of water in the atmosphere is generally greatest near the sea shore, for, owing to changes in temperature, much of the water will be precipitated before the moisture laden air can pass far inland. Drops of water collect on a cold surface, because the air in the immediate neighborhood is cooled to the point at which it is saturated with vapor. This point is called the dew point, and as the exact amount of water vapor which can be contained in a given volume of the atmosphere at any definite temperature is known, the discovery of the dew point affords a ready means of ascertaining the amount of moisture in the air. The ratio between the tension of the water vapor which would be found were the air fully saturated at the prevailing temperature and that tension which really exists, is called the relative humidity.* The quantity of water present in the atmosphere can also be ascertained by passing a known volume of air over weighed tubes filled with calcium chloride or any other substance which will readily absorb moisture, for then the gain in weight will give the exact amount of moisture which was present.

The water in the atmosphere is absolutely essential to plant life. The liquid falls upon the soil as rain and is then absorbed by the radicles; afterward it circulates through the entire system of the plant, taking part in various physiological changes and finally evaporating from the leaves. The amount of moisture which passes from large areas covered by vegetation is enormous, so that wooded districts cause an equitable distribution of rain.

Another impurity present in the atmosphere is ammonia, which, however, is always found combined with acids as ammonium carbonate, nitrate or nitrite. These substances are washed into the soil by the rain and are then taken up by plants to form those portions of their tissues which, in addition to carbon hydrogen and oxygen, also contain nitrogen, so that ammonium compounds are an essential constituent of the atmosphere; yet the amount of these is very small and variable, the greatest quantity ever found has been 47.6 parts by weight, in one million of the atmosphere. Small quantities of other impurities, such as sulphur dioxide and sulphuretted hydrogen, may occur in restricted areas where such gases are being formed, as, for instance, in districts where large quantities of sulphur bearing coal are burned. Ozone is also at times present in the atmosphere.

The solid particles floating in the air as dust may be of two kinds, inorganic and organic. Sodium chloride is always present in the inorganic particles, the organic substances may be of the greatest variety and frequently contain micro-organisms which can inaugurate disease.

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* By vapor tension at a given temperature is meant the pressure, in millimeters of the barometer, which is exerted by a vapor at that temperature.

The pressure which the atmosphere is exerting, by reason of its weight, is measured by the barometer. In the 17th century some Florentine pump makers, wishing to convey water to a very great height by means of a long suction pump, discovered to their chagrin that, no matter how great their exertions, the water would not follow the piston for more than thirty-two feet and so Galileo Galilei was appealed to for an explanation. The cause assigned to this phenomenon by the great man was, however, entirely a wrong one, for he maintained that a column of water longer than thirty-two feet would be broken by its own weight, just as would a bar of iron of sufficient length; therefore, water could never be pumped to any great height. Torricelli, a pupil of Galileo, soon after (1643) found the right explanation. He reasoned that when the pump created a vacuum the water was pressed upward by the weight of the atmosphere; if this were so, the height of a column of a specifically heavier liquid, such as mercury, which the atmosphere would sustain should be proportionally less. Accordingly, Torricelli filled a glass tube, sealed at one end, with mercury, closed the other with his thumb and, inverting the tube, placed the open end in a vessel filled with the same metal; the column of mercury then sank until its upper surface was between 28 and 29 inches above the level of the liquid in the trough, so that a vacuum was produced in the upper part of the tube. The experimenter now concluded that the weight of the column of mercury in the tube must be equal to the weight of a column of water with an equal cross section and a height of thirty-two feet, while both columns exerted a pressure which was opposed by an equal one produced by the atmosphere acting on the surface of the liquid in the open vessels in which the tubes were placed. If this conclusion was correct the height of a column of mercury which could be sustained by the atmosphere would be less on the monntain tops than on the low lands, and so Pascal, hearing of Torricelli's experiment, sent his brother-in-law Perrier, with a barometer, to an altitude of 5,000 feet, and the observer reported that at that elevation the mercury stood three inches lower than it did in Paris. The whole matter was now clear, the atmosphere exerted a pressure which could be measured by the height of the column of mercury it could sustain, while the instrument constructed with this end in view subsequently became known as the barometer.

The distance from the upper level of the mercury in the barometer tube to that in the vessel underneath, is the height of the barometer; at the level of the sea the average is 760 m. m. and in all scientific work this is taken as the standard for barometric measurements; as the weight of a column of mercury 760 m. m. long and with one square inches cross section is 15 pounds, it follows that the pressure exerted by the atmosphere is 15 pounds to the square inch. We do not feel this enormous weight because the air presses equally in all directions and because the pressure from within our bodies counterbalances that from without.

The volume occupied by any gas is inversely as the pressure exerted on it. Double the pressure and you halve the volume, quadruple the pressure and the volume will be one-fourth, and so on. If V_0 and V_t be the volumes of a gas at the same temperature but under different pressures, P_0 and P_t, then:

$$1.\quad V_0 : V_t :: P_t : P_0$$

$$2.\quad V_0\,P_0 = V_t\,P_t$$

now if P_0 is the standard barometric pressure of 760 m. m., then:

$$3.\quad V_0 = \frac{V_t\,P_t}{760},$$

or, the volume of a gas at standard pressure is equal to the volume at the existing pressure multiplied by that pressure in millimeters and divided by 760; but the existing pressure is the pressure of the atmosphere measured by the height of the barometer, h, ($P_t = h$) so that:

$$4.\quad V_0 = \frac{V_t\,h}{760}$$

All gases, when not very near the point at which they become liquid, expand $\frac{1}{273}$ of their volume for each degree of temperature* so that a liter of gas at 0° will be $1 + \frac{1}{273}$ liters at $+1°$ and $1 + \frac{10}{273}$ at 10°, and ten liters would be $10 + \frac{10}{273}$ at $+1°$, consequently:

$$5.\quad V_t = V_0 + V_0\,\alpha\,t. \qquad 6.\quad V_t = V_0(1 + \alpha\,t). \qquad 7.\quad V_0 = \frac{V_t}{1 + \alpha\,t.}$$

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* More accurately .00366.

where V_0 is the volume of any gas at 0°, V_t the volume of the same gas at any temperature, t is that temperature and $\alpha = \frac{1}{273}$. Uniting 3 and 7 in one equation, we have:

$$8. \quad V_0 = \frac{V_t\, h}{760\,(1 + \alpha\, t)}$$

so that the volume of any gas observed at 0° and 760 m. m. is equal to the volume multiplied by the height of the barometer and divided by 760 times, one plus $\frac{1}{273}$ of the temperature. If the gas to be measured is in a eudiometer tube,* partially filled with mercury, the pressure under which it is, is naturally not that of the atmosphere, but of that pressure minus the height of the column of mercury in the tube. If this height in millimeters be called w, then:

$$9. \quad V_0 = \frac{V_t\,(h - w)}{760\,(1 + \alpha\, t)}$$

and furthermore, if the gas is saturated with water vapor, the tension of water-vapor in millimeters, at the temperature of observation, must also be deducted from the barometric measurement. When the relations between volumes of gases are considered these are supposed to be under standard conditions, at 0° and 760 m. m. pressure.

The height of the barometer at any place is constantly undergoing variations, for the atmosphere is always subject to more or less serious local disturbances which affect the pressure exerted by it. The depth of the atmosphere is uncertain; it has been variously given at from thirty to two hundred miles. As the pressure is greatest on the surface of the earth, the air must be densest at this point, and must diminish in density the higher the altitude. Probably at an elevation of ten miles the pressure of the atmosphere would be imperceptible. The temperature of the air becomes less the greater the distance from the earth. The specific weight of the air at 760 m. m., and 0°, being the most frequently used standard of measurement, is generally taken as unity. Sometimes, however, gases are measured with hydrogen as the standard, when the specific gravity of air becomes 14.38 (hydrogen = 1) or 28.76 (hydrogen = 2). In order, therefore, to find the specific gravity of any gas with hydrogen as one, we must multiply the specific gravity referred to air by 14.38.

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* See Figure 13.

All living organisms upon the earth depend upon the atmosphere. Its oxygen, its carbon dioxide, its ammonia and its water-vapor are necessary to all forms of life, for those constituents which cannot be directly used by animals do indirectly find their way into their systems. The air is inspired by animals, its oxygen is absorbed, comes in contact with every tissue in the body and is exhaled, charged with carbon dioxide and water-vapor after its oxidizing action is completed. The plants make use of the carbon dioxide which finds its way into the atmosphere; when in the sunlight they assimilate it and thus form the greater portion of their tissues, but plants, as well as animals, require oxygen for their existence; neither can plants live without the presence of compounds of nitrogen, for many of their most essential chemical constituents, such as the albumens, are composed chiefly of carbon, hydrogen, oxygen and nitrogen. A little of this nitrogen may possibly be taken directly from that which is contained in the atmosphere; but certainly the major portion is furnished by compounds of nitrogen found in the soil. These compounds would soon be entirely used up were it not for their constant renewal by the addition of those which, originally in the atmosphere, are washed to the ground by rains and by such as are produced in the soil by the decay of organic substances. The plants are thus able to build their tissues from the simplest inorganic materials—from carbon dioxide, water, ammonium nitrates and nitrites. Animals have no such power; they destroy, where plants create. Some live upon plant substances and assimilate the ready-formed, complicated organic compounds; others prey upon each other, so as to get the compounds second-hand; they all die and, by decaying, once more return to the soil and air those substances which the plants had used; thus a ceaseless rotation of the life-supporting constituents of the atmosphere is going on, while the energy necessary to cause these metamorphoses is furnished by the heat and light of the sun.

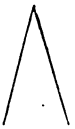
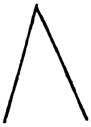
CHAPTER XXV.

COMPOUNDS OF THE ELEMENTS OF THE NITROGEN FAMILY.

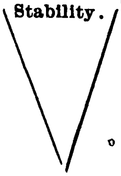
The elements of the nitrogen family are:

Nitrogen,	atomic	weight	14.03
Phosphorus,	"	"	31.
Arsenic,	"	"	75.
Antimony,	"	"	120.
Bismuth,	"	"	208.9

The same changes in the physical characteristics of the elements which, with increasing atomic weight, were observed in the halogene and in the sulphur families, are repeated in that group of elements of which nitrogen is a representative. This will be seen from the following table:

F,	O,	N, colorless gases.	Specific gravities.	Melting points.
Cl, yellow gas,	S,	P, yellow, easily fused, solids.		
Br, brown liquid,	Se,	As, metallic appearing solids.		
I, black solid,	Te,	Sb, silver white appearing solids		
—	—	Bi, reddish metallic solid.		

HYDROGEN COMPOUNDS.

FH	OH_2	NH_3	Stability. 	General formula of hydrogen compounds of halogenes, HX. General formula of hydrogen compounds of sulphur group, H_2X. General formula of hydrogen compounds of nitrogen group, H_3X. Valence of the elements of the halogene family toward hydrogen is 1. Valence of the elements of the sulphur family toward hydrogen is 2. Valence of the elements of the nitrogen family toward hydrogen is 3.
ClH	SH_2	PH_3		
BrH	SeH_2	AsH_3		
IH	TeH_2	SbH_3		

In this family, as well as in the other two which we have studied, the elements, as the atomic weight increases, change into substances entirely metallic in appearance, and what is more, the alteration is even more fundamental in its character, for the chemical as well as the physical properties of the last two elements in this group are more metallic than not-metallic. Once more we come in contact with a group of elements in which the one with the smallest atomic weight is a colorless gas, that with next higher a yellow solid easily fused and easily burned, while the next is a greyish white solid with the appearance of a metal and the chemical behavior of a not-metal, for in this respect arsenic is entirely like tellurium. Antimony and bismuth are metallic both physically and chemically, but while antimony shows a not-metallic nature in some of its compounds, bismuth is always a metal. The melting points of the elements in this family increase with the atomic weight, exactly as was the case in the sulphur and halogene families.

All of the elements belonging to the nitrogen group, with the exception of bismuth which is too much of a metal to do so, form gaseous hydrogen compounds which, following the general rule, diminish in stability as the atomic weight of the characterizing element increases. These compounds are formed by union of three hydrogen atoms to one of the nitrogen-like element—so that their general formula is $H_3 X$, while the valence of the joining element is three. By comparing all of the elements in the halogene, sulphur and nitrogen groups, we can see that, as the atomic weights of the families as a whole diminish, the valences toward hydrogen increase.

	F.	O.	N.
At. wt.	19	16	14
	Cl.	S.	P.
At. wt.	35.5	32	31
	Br.	Se	As
At. wt.	80	79	75
	I.	Te.	Sb.
At. wt.	127	125	120
Atomic wts.			

F H.	O H_2	N H_3
Cl H.	S H_2	P H_3
Br H.	Se H_2	As H_3
I H	Te H_2	Sb H_3
Valence I.	II.	III.
		Valence.

As we pass from one element to another corresponding one to the right of it, there is a diminuation of not more than five units in the atomic weight and an increase of one in the valence. No elements exist, the atomic weights of which lie between any two on the horizontal lines, so that these twelve elements form a portion of the natural grouping obtained by arranging the elements in the order of their atomic weights.

The hydrogen compounds of the elements of the nitrogen family show a chemical character which differs from that found in the other two because of the greater number of hydrogen atoms contained in them. The hydrogen compounds of the halogenes were acids, because one atom of each of those elements could unite with but one atom of hydrogen, the positive character of the latter therefore was not sufficient to counterbalance the negative properties of the halogene. The elements of sulphur family formed but slightly acid hydrogen compounds, for the two hydrogen atoms contained in these had twice the effect of the one in the chlorine group, while lastly the hydrogen compounds of theelements of the nitrogen family are either basic or neutral, for here the three hydrogen atoms entirely counterbalance the chemical character of that of the element with which they are united. However, an atom of hydrogen has a small mass, so that its influence on the character of a compound would become less as the mass of the atom of the element with which it is united becomes greater. This connection between mass and chemical character can be seen in the sulphur and nitrogen families; thus, water is nearly neutral in behavior, being both basic and acid; sulphuretted hydrogen, where the mass of the sulphur atom is twice that of an oxygen atom, has the power of reddening litmus, while its basic character is much less than that of water; lastly, hydrogen selenide and telluride are also weakly acid. In the nitrogen family; ammonia is a pronounced base, being capable of uniting with almost all acid substances to form stable compounds; $P H_3$ (phosphine) yields salts with but a few acids, such as H Br and H I, while $As H_3$ (arsine) and $Sb H_3$ (stibine) can form no salts; so that the increasing mass of the not-metallic element has gradually counterbalanced the effect of the positive hydrogen. Generalizations of this kind would be more simple were it not for the fact that another factor, that is, the diminishing not-metallic character of the elements with increasing atomic weights, influences the character of the hydrogen compounds. If iodine, for instance, were as negative as chlorine, we would expect hydroiodic acid to be a much stronger acid than hydrochloric, for the mass of an atom of iodine is greater than that of an atom of chlorine; that this is not the case is due to the fact that iodine is much less not-metallic in its character than is chlorine. Organic chemistry teaches us that if we substitute a more positive group of elements for the hydrogen contained in ammonia, the resulting compound becomes more like a metal, and that by substituting a less positive group it becomes less like a metal in its character, and also that arsine and stibine, which are neutral, can be made to act like metals if we only replace their

hydrogen atoms by groups of atoms having a more positive chemical character.*

Whatever truth there may be in the above considerations, the **facts** themselves are to be remembered; so that:

Compounds $H\,X$ of the halogenes are acid.

Compounds $H_2\,X$ of the sulphur group are acid (and sometimes basic).

Compounds $H_3\,X$ of the nitrogen group are basic or neutral.

In calling these compounds acid, we mean that they react with bases to form salts or salt-like bodies, in calling them basic that they can unite with acids to form similar substances. The following reactions will make this clear:

$$\begin{array}{llll} H\,Cl & + \quad K\,O\,H & = K\,Cl + H_2\,O. & \\ H_2\,S & + \; 2\,K\,O\,H & = K_2\,S + 2\,H_2\,O. & \\ \text{Acid.} & \quad \text{Base.} & & \end{array}$$

$$\begin{array}{llll} H_3\,N & + \quad H\,Cl & = N\,H_4\,Cl. \\ H_3\,N & + \quad H_2\,S & = N\,H_4\,S\,H. \\ \text{Base.} & \quad \text{Acid.} & \end{array}$$

Water can sometimes act like a base, as is seen from its behavior when it unites with anhydrides; this will be apparent by comparing the following two equations:

$$\begin{array}{lll} S\,O_3 & + \; H_2\,O = H_2\,S\,O_4 & \\ S\,O_3 & + \; K_2\,O = K_2\,S\,O_4\dagger & \\ \text{Anhydride.} & \quad \text{Base.} \qquad \text{Salt.} & \end{array}$$

One great difficulty in attempting a classification like this is found in the necessity of using such terms as "basic" and "acid," which are arbitrary and often differently applied by different chemists; this is somewhat obviated, for the present, by remembering that it is only the general chemical characteristics shown by the hydrogen compounds of the not-metals, which we are considering; when the student subsequently discovers, for instance, that the hydrogen atoms in ammonia can be replaced by potassium, he need not for that reason look upon the compound as an acid—for this would only be an individual case, and then, the resulting potassium compound does not have the general characteristics of a salt. (See page 71.)

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* A "positive" element is one which in a given chemical compound behaves like a metal, a negative element is one which behaves like a not-metal, while positive and negative groups are such as can chemically show the same contrast to each other as do a metal and a not-metal.

† See pages 28 and 29.

All of the elements of the nitrogen family form oxides, the general formulæ of the most important of which, together with those of the acids derived from them, are given on the following table; those of the corresponding halogene compounds are repeated for purposes of comparison:

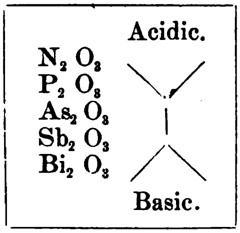
HALOGENES.		Valence.	NITROGEN FAMILY.			In the nitrogen family, the acids HXO_2 and HXO_3 can (excepting the nitrogen acids) form stable hydrated acids:
Oxides.	Acids.		Oxides.	Acids.	Nomenclature.	
X_2O	HXO	1	——	——	Hypo-ous acid	
X_2O_3	HXO_2	3	X'_2O_3	$HX'O_2$	——ous acid	
X_2O_5	HXO_3	5	X'_2O_5	$HX'O_3$	——ic acid	$HX'O_2+H_2O=H_3X'O_3$
(X_2O_7)	HXO_4	7	——	——	Per—ic acid	$HX'O_3+H_2O=H_3X'O_4$

The trioxides and the pentoxides, as well as the acids derived from them by the addition of water, have the same formulæ in both families, while the nomenclature of the acids is also the same, thus:

Cl_2O_3 yields $HClO_2$, chlorous acid, and N_2O_3 yields HNO_2, nitrous acid.

I_2O_5 yields HIO_3, iodic acid, and N_2O_5 yields HNO_3, nitric acid.

There are no important acids in the nitrogen family corresponding to hypochlorous and hypobromous acids, and as the highest valence of the elements of this group toward oxygen is five, there can be none corresponding to perchloric acid, which is derived from chlorine with a valence of seven. All of the elements of the nitrogen family, with the exception of nitrogen and bismuth, have a great tendency to form hydrated acids which are much less readily decomposed than are those of the corresponding class in the other two families. As a consequence, phosphorous acid exists, not as HPO_2, but as H_3PO_3 ($HPO_2 + H_2O$), and phosphoric acid as H_3PO_4 ($HPO_3 + H_2O$) more often than as HPO_3, so that the acids most frequently met with contain the same number of hydrogen atoms in a formula weight as there are in a molecule of ammonia. The oxide X'_2O_3 becomes more basic as the atomic weight of X' increases, so that, while N_2O_3 and P_2O_3 are the anhydrides of acids, As_2O_3 is both a base and an anhydride, Sb_2O_3 is more basic than acidic, while Bi_2O_3 acts altogether as a base. This change in the nature of the oxides is the natural result of the change from not-metal to metal which takes place in this family.



The pentoxides, $X'_2 O_5$, all are anhydrides of acids with no basic properties;* therefore, an addition to the amount of oxygen present in the compounds which are basic changes the latter into more negative and, as a consequence, acidic bodies. The general rule is that where several oxides of the same metal exist, the character of these becomes less basic as the number of oxygen atoms increases, so that frequently the lowest oxide may be a strong base, forming most stable salts with acids, while the highest may be the anhydride of an acid; as a consequence, the oxides of the same element may not resemble each other as much as they do the corresponding oxides of some other element.

Nitrogen, in addition to the two oxides, $N_2 O_3$ and $N_2 O_5$, forms three others, $N_2 O$, $N O$ and $N O_2$, which will be discussed at the proper time. The chlorides of the elements of the nitrogen family have the general formulæ $X' Cl_3$ and $X' Cl_5$; their stability increases as the metallic character of the elements becomes more pronounced:

$N Cl_3$ (?), explosive.

$P Cl_3$, $P Cl_5$, decomposed by water to phosphorous and phosphoric acids.

$As Cl_3$, ——, exists in the presence of little water, entirely decomposed by much water.

$Sb Cl_3$, $Sb Cl_5$, partially decomposed by water.

$Bi Cl_3$, ——, partially decomposed by water.

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* $Bi_2 O_5$ shows scarcely any of the properties of an anhydride, the compound $H Bi O_3$, corresponding to $H N O_3$, has been isolated. but it forms no salts and shows a tendency to break down, giving off oxygen.

CHAPTER XXVI.

AMMONIA AND THE OTHER COMPOUNDS OF NITROGEN AND HYDROGEN.

Ammonia: $N\,H_3$. *Specific weight, air = 1, is .589, H = 2 is 16.96, molecular weight 17. 1 cc. at 0° and .76 m. pressure, weighs .0007635 gram.*

Ammonia is by far the most important of the three compounds of nitrogen and hydrogen. It is never found, as such, in nature but always occurs as an ammonium salt, combined with some acid; in the atmosphere and soil it is found as ammonium carbonate, nitrite and nitrate; in mineral waters and in volcanic regions, as the sulphate. Ammonium compounds occur in almost all plants, in the air exhaled from the lungs, and in the urine of animals. Those ammonium compounds which are found in the soil and in clay are produced from outside sources.

Salts of ammonium were first introduced into Europe from Eastern countries, especially from Armenia, so that the name given by the Arabian alchemists to the chloride, the salt which earliest came into prominence, was *sal armeniacum*, but this term was subsequently altered to *sal ammoniacum*, which had been given to sodium chloride imported from the neighborhood of the temple of Jupiter Ammon in the Libyan Desert. The earliest ammonium compounds were prepared in the East by the distillation of camel's dung and were much prized as universal remedies; subsequently other animal refuse was used in the preparation of the carbonate; at one time the substance prepared by the dry distillation of harts' horns was considered the most potent, so that the name, spirits of hartshorn, is still used to designate a solution of ammonia in water. No distinction was made between ammonia and the carbonate of ammonium, both were called volatile alkali, until Priestley collected pure ammonia gas over mercury. The term ammoniaque was introduced by the French chemists at the close of the last century, and from this our term ammonia has its origin.

Nitrogen and hydrogen have no tendency whatever to unite under ordinary circumstances, only if electric sparks are allowed to pass for some time through a mixture of the two gases does union take place. If, however, hydrogen acts upon some oxide of nitrogen under proper conditions, especially if the hydrogen is in the so-called nascent state, ammonia is formed with the greatest ease. For instance, if a mixture of nitric oxide ($N\,O$) and hydrogen are passed through a tube heated to dull redness and containing a few pieces of spongy platinum, ammonia and water are produced:

$$N\,O + 5H = N\,H_3 + H_2\,O.$$

If pieces of iron or zinc act upon very dilute nitric acid, ammonium nitrate is produced, the hydrogen which first results from the action of the metal on the acid not only takes away all of the oxygen from the compound of nitrogen which it attacks, but even, in addition, unites with that element to form ammonia. (See nitric acid.) Decaying organic substances which contain nitrogen, give off ammonia, which, uniting with the carbon dioxide formed at the same time, produces ammonium carbonate; the odor of ammonia can therefore be detected in the neighborhood of heaps of manure or in stables. The compounds of nitrogen which are an essential constituent of existing plants and animals, must have been just as necessary in past geologic eras, so that those remains which are found as bituminous coal are rich in compounds of carbon, hydrogen, oxygen and nitrogen; the dry distillation of this coal at present produces nearly all of the ammonia in use. When bituminons coal is heated without the access of air a large number of commercially extremely important products are given off. They are:

Gaseous—Illuminating gas, ammonia, sulphuretted hydrogen.

Liquid—Water, benzol, toluol, phenol, etc.

Solid—Naphthalene, anthracene, etc.

The highest boiling products are substances like asphalt, while the carbon remains behind in the form of coke.

The ammonia which passes from the gas manufacturing retorts is collected by passing the mixture of gases upon surfaces of wood over which a continuous stream of water is trickling; the solution so formed is a dark colored liquor from which it is an easy matter to obtain ammonia in a pure state. To do this, the dissolved ammonia is converted either into ammonium chloride or sulphate by the addition of hydrochloric or sulphuric acid. The solution of ammonia in water we may presume contains the gas combined with water as ammonium hydroxide:

$$NH_3 + H_2O = NH_4OH.$$

When acids are added to this hydroxide, an ammonium salt is produced, just as a potassium or sodium salt would be formed under similar circumstances:

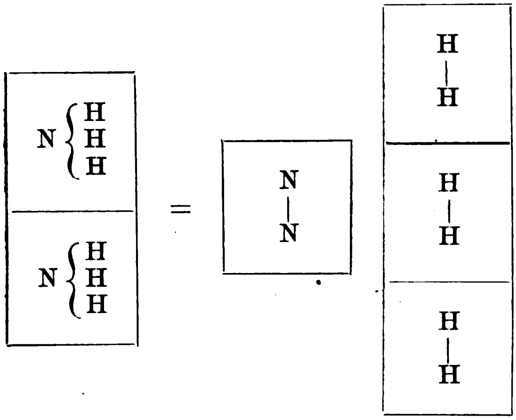
$$\begin{aligned} KOH + HCl &= KCl + H_2O, \\ 2\,KOH + H_2SO_4 &= K_2SO_4 + 2\,H_2O, \\ (NH_4)OH + HCl &= (NH_4)Cl + H_2O, \\ 2\,(NH_4)OH + H_2SO_4 &= (NH_4)_2SO_4 + 2\,H_2O, \end{aligned}$$

for the group of elements NH_4 acts exactly like sodium or potassium. In order to liberate the ammonia from these salts it is only necessary to treat them with some such base as sodium or calcium hydroxide, for these not-volatile bases would expel a volatile one from its salts, so that:

$$\begin{aligned} NH_4Cl + NaOH &= NaCl + NH_4OH. \\ (NH_4)_2SO_4 + 2\,NaOH &= Na_2SO_4 + 2\,NH_4OH, \\ 2\,(NH_4)Cl + Ca(OH)_2 &= CaCl_2 + 2\,NH_4OH; \end{aligned}$$

The ammonium hydroxide so formed breaks down into ammonia and water, $NH_4OH = NH_3 + H_2O$, so that pure ammonia gas can be liberated from the chloride or sulphate of ammonium formed, as shown above, by acidifying the crude ammoniacal liquor. The gas is then collected by passing it into water and the solution so formed is the *liquor ammonia* of commerce. A similar method can be employed in the production of small quantities of ammonia for laboratory use.[48]

Ammonia is a colorless gas with a penetrating alkaline odor. At -40° and under a pressure of one atmosphere, it condenses to a colorless liquid which boils at -38.5° and which changes into a crystalline solid at -75°. The gas has a specific gravity of .596 at 0° and 760^{mm}, which, with hydrogen as two, gives a density of 16.9, so that the molecular weight of this compound is 17. As a consequence we can collect the gas by upward displacement, exactly as was done with hydrogen. Ammonia is quite a stable compound, just as were the corresponding substances in the oxygen and halogene families, namely, water and hydrofluoric acid; it follows that ammonia does not support combustion and burns with difficulty to form water and nitrogen, even when it is mixed with oxygen and ignited.[49] Naturally it does not support life. The gas can be completely decomposed into nitrogen and hydrogen by passing an electric spark through it for some length of time, and, when this is done, two volumes of ammonia yield three of hydrogen and one of nitrogen.



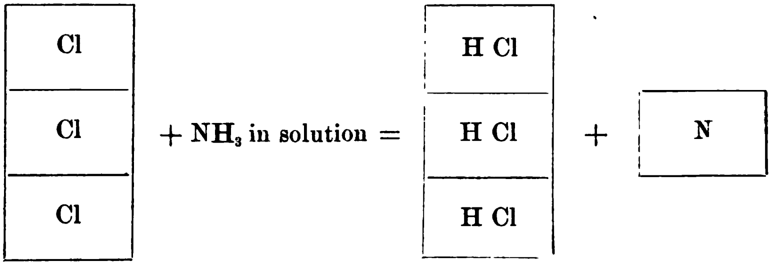
or $2\,NH_3 = N_2 + 3\,H_2$.

Ammonia, when it is heated to 780° in a porcelain or iron tube, is almost completely dissociated into hydrogen and nitrogen.

Ammonia can, under proper circumstances, burn in oxygen to form water and nitrogen, and just so it is acted on by chlorine to form hydrochloric acid and nitrogen:

$$NH_3 + 3\,Cl = N + 3\,H\,Cl.$$

By means of this reaction we can readily determine the relative volumes of nitrogen and hydrogen which go to make ammonia. If we fill a long glass tube with chlorine and then add ammonia water without admitting any air, hydrochloric acid and nitrogen will be formed. We learned that one volume of chlorine unites with one volume of hydrogen to form hydrochloric acid, so that the volume of chlorine in the vessel must have united with an equal volume of hydrogen which was contained in the ammonia water, and therefore the volume of hydrogen which was present in the ammonia is given by the volume of chlorine in the vessel. Now, by cautiously admitting very dilute sulphuric acid, we can absorb the excessive ammonia, while the hydrochloric acid has already formed ammonium chloride with the ammonia water. Nothing but nitrogen will therefore remain in place of the chlorine originally used, and its volume will exactly fill one-third of the tube. It follows that one volume of nitrogen and three of hydrogen unite to form ammonia. The following diagram will make this clear:



The H Cl is removed by dissolving in ammonia water, so that the N remains, and this must be one-third the original volume of chlorine.

We have seen that when ammonia is decomposed by the electric spark, two volumes of the gas yield three of hydrogen and one of nitrogen, and that, conversely, ammonia is formed from three volumes of hydrogen and one of nitrogen. From the first of these two discoveries we can conclude, as we did in the case of oxygen and chlorine, that nitrogen contains two atoms in its molecule (see page 68), from both we conclude that the formula of ammonia is NH_3. In addition, the specific gravity of ammonia shows us that its molecular weight is 17, and quantitative analysis that in seventeen parts by weight of ammonia there are fourteen of nitrogen and three of hydrogen. The atomic weight of nitrogen is therefore presumably 14, and must remain so unless some compound of nitrogen should be discovered, the molecular weight of which is known and which contains less than fourteen parts by weight of nitrogen.

Ammonia is very soluble in water, one volume of water dissolves 813 times its own volume of ammonia gas.[50] The solution has the odor of ammonia gas, is alkaline, for it changes red litmus to blue, and is generally considered as containing the ammonia combined with water in the form of ammonium hydroxide, NH_4OH.* Upon warming the solution, ammonia is expelled, and this fact is made use of in the preparation of artificial ice. An iron vessel containing ammonia water is connected by pipes with another one in the form of a double walled hollow cylinder, all of the connections being such that no gas can escape. Ammonia water is placed in the first vessel and is warmed. The escaping gas passing into the space between the double walls of the second vessel, which is cooled by means of cold water. The pressure of ammonia and the cold, combined, condense the gas to a liquid. The conditions are now reversed, the cylinder is slightly warmed, while the first vessel is cooled, the condensed gas boils and is absorbed by the water contained in the latter, while, when the liquid ammonia boils, enough heat is absorbed to freeze a can of water placed within the hollow cylinder.

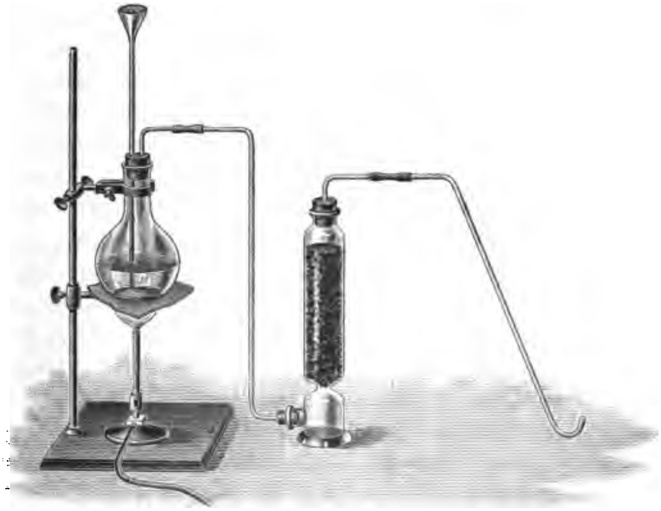


FIGURE 35.

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* According to recent investigations it seems probable that ammonium hydroxide is not formed when ammonia dissolves in water, for all other hydroxide solutions conduct electricity with as great ease as salt solutions, but the solution of ammonia in water has only $\frac{1}{10}$ the conducting power of a salt of the same molecular weight. As all of the salts of ammonium correspond to those of potassium, it is however convenient to consider the solution of ammonia in water as ammonium hydroxide,

Ammonia gas can add itself directly to acids, forming salts as follows:

$NH_3 + H\,Cl = NH_4\,Cl$ ammonium chloride,
$2\,NH_3 + H_2\,SO_4 = (NH_4)_2\,SO_4$ " sulphate,
$NH_3 + H\,NO_3 = NH_4\,NO_3$ " nitrate.

These salts are called *ammonium* salts, the group of elements NH_4, which acts exactly as does potassium, is called *ammonium*, it takes the place of hydrogen in the acids, and the salts so produced have exactly the character of the salts of the true metals. Where a group of elements acts in this manner, being transferred from one compound to another without decomposition, just as an element would be, it is called a radicle. Ammonium is, therefore, the unchanging constituent of a large number of compounds, if the grouping of elements NH_4 is destroyed, then ammonium salts lose their identity as such. Ammonium is a radicle which can act as a metal, we are acquainted with other radicles which are composed entirely of not metals and which act as much like the latter as ammonium does like the former, indeed, it is very difficult to say just what compounds shall be called radicles and what shall not be, but it is best to limit the term to such groups of elements as are very frequently met with as the unchanging constituents of a large number of compounds, and which can be transferred from one compound to another *as a whole*, and without alteration.

When ammonia dissolves in water, its solution, for convenience in chemical notation, is considered as one of the hydroxide of ammonium:

$$NH_3 + H_2O = NH_4\,OH.$$

With this hypothesis in view the parallelism between ammonium and the metals becomes more apparent for:

$$(NH_4)\,OH + H\,Cl = (NH_4)\,Cl + H_2O.$$
Ammonium hydroxide + hydrochloric acid = ammonium chloride + water.

$$KOH + H\,Cl = K\,Cl + H_2\,O.$$
Potassium hydroxide + hydrochloric acid = potassium chloride + water.

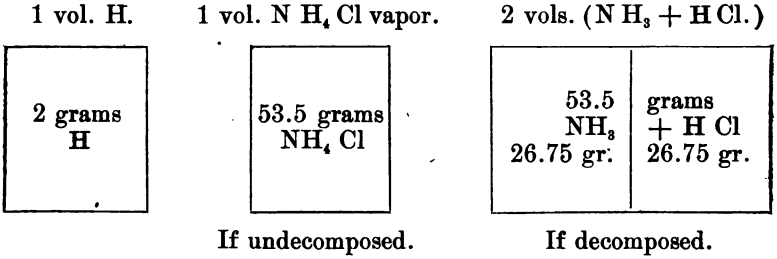
$$2\,(NH_4)\,OH + H_2\,SO_4 = (NH_4)_2\,SO_4 + 2\,H_2\,O.$$
Ammonium hydroxide + sulphuric acid = ammonium sulphate + water.

$$2\,K\,OH + H_2\,SO_4 = K_2\,SO_4 + 2\,H_2O.$$
Potassium hydroxide + sulphuric acid = potassium sulphate + water.

These salts, upon heating, decompose into ammonia and the corresponding acid. Thus ammonium chloride, when vaporized, yields ammonia and hydrochloric acid:

$$NH_4\,Cl = NH_3 + H\,Cl.$$

The specific gravity of ammonium chloride vapor, if hydrogen = 2, provided no decomposition had taken place, should be the same as its molecular weight, or 53.5. In reality it is only one-half of this number, or 26.75. Let us suppose a volume of hydrogen weighs two grams, then an equal volume of ammonium chloride vapor weighs 26.75 grams—but were it vaporized without decomposition then it should weigh 53.5 grams, it follows therefore that the ammonium chloride has decomposed into a molecule of ammonia and one of hydrochloric acid.*



These conclusions are a necessary result of Avogadro's hypothesis, (page 66). Quite a number of bodies dissociate into two simpler ones on vaporizing. All of these give abnormal specific gravities; for their vapors, but the explanation is always the same as that just given for ammonium chloride. The fact that the specific gravity of ammonium chloride vapor, if hydrogen is two, does not correspond to the molecular weight, does not invalidate the method of obtaining the molecular weights of gases by means of their specific gravities; it only shows us that we must be careful to ascertain if the gas, the specific gravity of which we are about to determine, is identical in chemical constitution with the liquid or solid from which it is produced.

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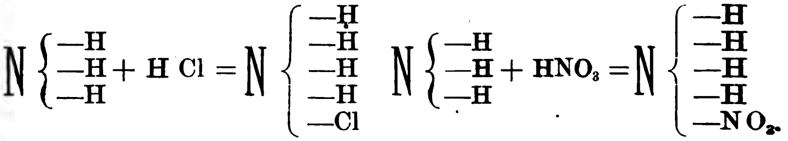
* Recently ammonium chloride has been vaporized under less than atmospheric pressure, in which condition no decomposition took place, as the specific gravity of the vapor indicated. The molecules of the gas had the formula NH^4 Cl. This proves that nitrogen is quinquivalent in ammonium chloride.

Nitrogen is trivalent in ammonia, but the element is unsaturated (see page 103); while it is not capable of taking up any more positive atoms, such as hydrogen, it can add other atoms, provided the group to be added contains a negative element or group of elements. Because the large number of hydrogen atoms contained in NH_3 have rendered that compound positive, it has no tendency to further unite with positive substances, but when a negative compound such as hydrochloric or any other acid is added to ammonia, the latter separates the former with two parts, namely into hydrogen and the not-metallic element or group of elements with which hydrogen was united, these two parts add separately, so that nitrogen becomes quinquivalent,



$$N\begin{cases}-H\\-H\\-H\end{cases}+H\,Cl=N\begin{cases}-H\\-H\\-H\\-H\\-Cl\end{cases}\qquad N\begin{cases}-H\\-H\\-H\end{cases}+HNO_3=N\begin{cases}-H\\-H\\-H\\-H\\-NO_2.\end{cases}$$

We have seen that water was similarly decomposed when adding to oxides to form hydroxides (see page 111, 112).

All ammonium salts are decomposed by heat, with the following results:

1. The ammonium salts may be entirely disintegrated, as is the case with ammonium nitrate, for when that substance is heated neither ammonia nor nitric acid are produced.
2. Ammonia and the acid are produced.
    a. The acid may be volatile, then nothing remains.
    b. The acid may be not-volatile. then it remains.
    c. The acid may be decomposed by heat, then its decomposition product remains.

The radicle NH_4, ammonium, has never been isolated, but it appears that it can act like a metal in forming an amalgam with mercury. If an ammonium salt, like ammonium chloride, is decomposed by sodium in the presence of mercury, the ammonium liberated will form an amalgam with the latter.*

$$NH_4\,Cl + Na = NH_4 + Na\,Cl.$$

The mercury will expand and become of the consistency of soft butter. This amalgam gradually decomposes, ammonia and hydrogen are given off, and the mercury shrinks to its former size.[51]

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* Amalgams are solutions of metals in mercury. They sometimes have definite crystalline forms or definite quantities of metal and mercury. The mercury may in these possibly play the part of water of crystallization.

Nitrogen forms two other compounds with hydrogen, namely hydrazine, $N_2 H_4$ and azoimide, $N_3 H$, both of these substances were recently discovered by Curtius. Hydrazine can be considered as analogous to hydrogen dioxide, for the latter is water in which one atom of hydrogen if replaced by hydroxyle:

$$H-O-H \text{ and } HO-OH,$$

while the former is ammonia in which one atom of hydrogen has been replaced by the univalent group $-NH_2$,

$$H-N=H_2 \text{ and } H_2=N-N=H_2,$$

the group of atoms to which hydrogen is attached is in the one case $-O-O-$ and in the other $=N-N=$; as oxygen is bivalent, each oxygen atom in the above group will only be capable of uniting with *one* hydrogen atom while, as nitrogen is trivalent, each nitrogen atom is capable of further union with *two* hydrogen atoms. (See pages 102, 103).

Hydrazine is a colorless gas which has scarcely any odor when inhaled in small quantities; it is quite soluble in water, its solution turns red litmus blue and the gas forms white clouds with hydrochloric acid, just as ammonia would do. Hydrazine is therefore basic in its character, so that it, like ammonia, unites with acids to form salts. These salts have the same composition as those of ammonium, with the exception that one atom of hydrogen is replaced by the univalent radicle $-NH_2$.

$$N\left\{\begin{array}{l}H\\H\\H\\H\\Cl\end{array}\right. \qquad\qquad N\left\{\begin{array}{l}H\\H\\H\\-NH_2\\Cl\end{array}\right.$$

Ammonium chloride. Hydrazonium chloride.

Both of the radicles NH_2 contained in hydrazine can, however, unite with acids, so that the salts might be considered to be formed as follows:

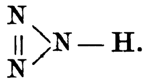
$$NH_2-NH_2+H\,Cl = NH_2-NH_3\,Cl,$$
$$H\,Cl+NH_2-NH_3\,Cl = NH_3\,Cl-NH_3\,Cl.$$

In hydrazine we would therefore have a diacidic base, just as in sulphuric acid we have a dibasic acid.

Azoimide or hydrogen nitride, N_3H, is a colorless gas with a peculiar, very penetrating odor, it is quite poisonous and its solution in water has an extremely irritating effect upon the skin. The most interesting fact in regard to this compound is that it is a strong acid, greatly resembling hydrochloric or hydrobromic acids, but a short consideration will show us the reason for this chemical behavior, for in azoimide the mass of the three nitrogen atoms entirely overbalances that of the one hydrogen atom, and consequently the compound, as a whole, is negative (see pages 172, 173); we would therefore expect azoimide to be acid in its nature.[*] Azoimide forms dense white fumes with ammonia, just as hydrochloric acid does, the substance formed in the one case is ammonium nitride just as in the other it was ammonium chloride:

$$\begin{aligned} NH_3 + HN_3 &= NH_4N_3, \\ NH_3 + HCl &= NH_4Cl. \end{aligned}$$

The solution of azoimide attacks copper, aluminium, zinc and other metals, forming the nitrides and liberating hydrogen; it dissolves oxides and hydroxides of metals. The nitrides formed, in all cases, resemble the corresponding chlorides. Hydrogen nitride differs from hydrogen chloride only because it is very explosive, for even a shock or a slight increase in temperature will cause it to explode with terrific force. It follows from this that the grouping of three nitrogen atoms in this molecule only takes place under great tension, so that the molecule is subjected to a constant strain, just as a wound up watch spring is. The structural formula assigned to hydrogen nitride by its discoverer is:



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[*] As we increase the number of hydrogen atoms in the three compounds of nitrogen and hydrogen, and as at the same time we diminish the number of nitrogen atoms, we pass from an acid to bodies with an entirely opposite chemical character. This change reminds us of the transition from not-metals to metals which we encountered in the natural families formed by the elements which we have studied —with the difference that with the increase of the mass of the not-metallic element in these compounds, the negative properties *increase* while in a natural family they *diminish*.

CHAPTER XXVII.

THE COMPOUNDS OF NITROGEN WITH OXYGEN AND WITH OXYGEN AND HYDROGEN.

Nitrous oxide, $N_2 O$, specific gravity, air = 1, is 1.527, H = 2, is 43.97, molecular weight is 44. 1 c.c. of the gas weighs .0019835 gram at 0° and .76 m. pressure. Nitric oxide, $N O$, specific gravity, air = 1, is 1.0384, H = 2, is 29.9, molecular weight is 30. 1 c.c. of the gas weighs .001348 gram. Nitrogen peroxide, $N O_2$, specific gravity, air = 1, is 1.59, H = 2, is 45.8 (at 130°) molecular weight is 46 (at 140°).

Nitrogen forms the following compounds with oxygen and hydrogen:

1.	$N_2 O$,	Nitrous oxide,	$H N O$, hyponitrous acid,
2.	$N O$,	Nitric oxide,	————————,
3.	$N_2 O_3$,	Nitrogen trioxide,	$H N O_2$, nitrous acid,
4.	$N O_2$,	Nitrogen peroxide,	————————,
5.	$N_2 O_5$,	Nitrogen pentoxide,	$H N O_3$, nitric acid.

Of these compounds, $N_2 O$, $N_2 O_3$ and $N_2 O_5$ are similar to those encountered in the study of the halogenes, for there we have $Cl_2 O$, $Cl_2 O_3$ and $I_2 O_5$, so that, provided we consider oxygen as being uniformly bivalent, the valence of nitrogen in these oxides is one, three and five; the acids derived from these three oxides, $H N O$, hyponitrous acid, $H N O_2$, nitrous acid, $H N O_3$, nitric acid also have formulæ like those of the halogene acids; but no pernitric acid exists, for the highest valence displayed by the nitrogen family is five. Nitric oxide does not act like the anhydride of an acid, it is but little soluble in water and is not attacked by bases; neither has nitrous oxide the characteristics of an anhydride, it has no tendency to form hyponitrous acid with water or hyponitrites with alkalis, but, on the other hand, it is produced when a solution of hyponitrous acid is warmed, so that it must be looked upon as the anhydride of that acid. We will begin the discussion of the oxides of nitrogen with nitrous oxide, following with nitric oxide, nitrogen trioxide, nitrogen peroxide and nitrogen pentoxide in the order named.

Nitrous oxide never occurs as such, it is solely a product of the laboratory. The gas was discovered by Priestley in 1776 and was first called dephlogisticated nitric gas, its composition was not explained until some time after its discovery, when Davy proved it to be an oxide of nitrogen. It is best prepared by heating ammonium nitrate, when water and nitrous oxide are formed as follows:[52]

$$NH_4NO_3 = N_2O + 2\,H_2O,*$$

but the gas can also be produced by the reduction of nitric oxide by means of finely divided metals, such as zinc or iron.

Nitrous oxide is a colorless gas with a very slight odor and sweetish taste. Its specific gravity, air = 1, is 1.527, which, with hydrogen as two, would give 44.96, so that the molecular weight is in round numbers, 44. In this weight, analysis shows that there are twenty-eight parts by weight of nitrogen and sixteen of oxygen, so that nitrous oxide contains, in its molecule, one atom of oxygen and two of nitrogen; for, by means of the study of water and other compounds of oxygen, we have concluded that the atomic weight of oxygen is sixteen, provided that of hydrogen is 1.007, and from our study of the composition of ammonia and other nitrogen compounds it follows that the atomic weight of nitrogen is 14. Nitrous oxide has, therefore, a structure similar to that of water, as will be seen by comparing the formulæ:

FIGURE 36.

$$N - O - N \text{ and } H - O - H.$$

Nitrogen is, therefore, univalent in nitrous oxide just as hydrogen is in water. From a further study of its composition we see that two volumes of nitrogen will unite with one of oxygen to form two volumes of nitrous oxide, just as two volumes of hydrogen united

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* A similar reaction takes place when ammonium nitrite is heated; only then *nitrogen* and not *nitrous oxide* is formed:

$$NH_4NO_2 = 2\,N + 2\,H_2O.$$

with one of oxygen to form two of water; the conclusions regarding the composition of water, at which we arrived on page 68, are consequently equally applicable to nitrous oxide.

Nitrous oxide is quite readily soluble in water, at 0° one volume of water will absorb about one hundred and thirty volumes of the gas. Nitrous oxide will support combustion almost as readily as oxygen does, a glowing pine chip will take fire in the gas and phosphorus as well as sulphur, which have been ignited in the air, will continue to burn brilliantly in nitrous oxide. The great tendency to give off oxygen which is displayed by nitrous oxide, is readily understood when we consider that it is an endothermic compound, in the formation of which work which is equivalent to 185 K must be done; the gas therefore posseses more energy than its constituents, and will break down at the first opportunity. That, however, considerable impulse is required to inaugurate this decomposition is shown by the fact that feebly burning sulphur is extinguished in the gas, while that which is combusting with considerable energy will continue to do so in nitrous oxide with almost the same brilliancy as if it were placed in oxygen. When a substance which, like phosphorus, forms a solid oxide, burns in nitrous oxide there is no change in volume, for the molecule of N_2O simply loses oxygen, while a molecule of N_2 is left in its place, one thousand molecules of nitrous oxide would therefore yield the same number of molecules of nitrogen, or x molecules of nitrous oxide would yield x molecules of nitrogen, it therefore follows that the volume of nitrogen which is formed has the same number of particles as the volume of gas from which it is produced, provided the gases have the same temperature and are under the same pressure, but, *when two gases, under the same temperature and pressure, contain equal numbers of molecules, they have equal volumes.*

Nitrous oxide is quite readily condensed to a liquid, at 0° it becomes fluid under a pressure of thirty atmospheres, its boiling point, under atmospheric pressure, is —88°, it becomes solid at —100°.

Although nitrous oxide can give up its oxygen so readily to burning substances, it cannot do so in order to support respiration. If the gas is inhaled, the first effect is loss of consciousness accompanied by a rumbling in the ears, while the person undergoing treatment experiences an involuntary tendency to laugh; as a consequence of this effect Davy named this substance laughing gas. Small animals are very rapidly killed by nitrous oxide. The effects of the inhalation of the gas disappear soon after pure air is taken into the lungs—and as a consequence it is extensively used as an anæsthetic in place of chloroform or ether. The nitrous oxide used for this purpose is condensed and transported in iron bottles.

Nitric oxide is the oxide of nitrogen which contains the next greater quantity of oxygen. It results from the action of many metals or, indeed, if other oxidizable substances on nitric acid; it does not occur in a free state, for the oxygen of the atmosphere converts it into a mixture of the two higher oxides, $N_2 O_3$ and NO_2. The most convenient method of preparing the gas is by the action of nitric acid on copper.[53] When copper is treated with nitric acid the first result, if we can reason from analogy, would most probably be the formation of copper nitrate and hydrogen:

$$\begin{aligned} Zn + H_2 SO_4 &= Zn SO_4 + 2 H, \\ Zn + 2 H Cl &= Zn Cl_2 + 2 H, \text{ and} \\ Cu + 2 H NO_3 &= Cu (NO_3)_2 + 2 H, \end{aligned}$$

Nitric acid, however, although it is much more stable than the chlorine, bromine and iodine acids which we have just considered, is nevertheless a powerful oxidizer, so that it changes the hydrogen evolved in the nascent state into water, and therefore, the result of this action would be that the nitric acid would lose oxygen, as follows:

$$1.\quad H NO_3 + 6 H = 4 H_2 O + 2 NO.$$

In order to produce the requisite hydrogen, the following reaction must take place:

$$2.\quad 3 Cu + 6 H NO_3 = 3 Cu (NO_3)_2 + 6 H.$$

So that (combining 1 and 2) the action of nitric acid on copper could be represented as follows:

$$3.\quad Cu + 8 HNO_3 = 3 Cu (NO_3)_2 + 2 NO + 4 H_2 O.$$

Other metals as well as copper, and reducing agents such as sulphur dioxide, will also produce nitric oxide from nitric acid. For instance, nitric acid oxidizes dry sulphur dioxide to sulphuric acid, while at the same time nitric oxide is produced. When nitric acid acts in this way the oxidizing action is always produced as follows:

a. $2\,HNO_3 = H_2O + 2\,NO + 3\,O$.

So that two formula-weights of nitric acid have three atoms of oxygen at their disposal, they can therefore oxidize three of sulphur-dioxide to sulphuric acid as follows:

b. $3\,SO_2 + 3\,H_2O + 3\,O = 3\,H_2SO_4$.

Combining a and b, we have:

c. $2\,HNO_3 + 3\,SO_2 + 3\,H_2O = 3\,H_2SO_4 + 2\,NO + H_2O$.

In all other cases where nitric oxide is produced from nitric acid, the reaction takes place in a manner similar to the above.

Nitric oxide is a colorless gas, which instantly turns dark brown on exposure to the atmosphere, nitrogen trioxide and nitrogen peroxide being formed; as a consequence there can be no experiment showing whether the gas is tasteless and odorless as well as colorless. The two gases produced by contact of nitric oxide with the air are poisonous. The specific gravity of nitric oxide is 1.04 when air is the standard, this corresponds to a density of 29.9, $H = 2$, or to a molecular weight of 30. It follows, as in this molecular weight there are fourteen parts by weight of nitrogen and sixteen of oxygen, that the formula of nitric oxide is NO. The gas is composed of equal volumes of nitrogen and oxygen, just as hydrochloric acid was of hydrogen and chlorine. If we wish to consider oxygen as bivalent, then nitrogen must also be bivalent in this compound. The specific gravity of nitric oxide does not change even at a temperature as low as —70°. At —153.6° and at atmospheric pressure, nitric oxide changes to a colorless liquid which solidifies at —167°, forming a snow-like mass. The gas is very stable; it can be heated to 1200° without alteration; at white heat it is completely broken down into nitrogen and oxygen. One hundred volumes of water dissolve about five volumes of nitric oxide at ordinary temperatures.

Nitric oxide does not allow substances to burn in it as readily as does nitrous oxide. For instance, melted phosphorous does not take fire in the gas unless it is burning at the same time; in the latter event, it will unite with the oxygen of nitric oxide with the greatest energy. On the other hand, sulphur, a burning candle or burning hydrogen are extinguished by nitric oxide. A mixture of carbon disulphide and nitric oxide burns with an exceedingly brilliant flame. Metals like zinc or iron, which are easily oxidized, will, if moist, readily remove a part of the oxygen from nitric oxide and in that way produce nitrous oxide:

$$2\,NO + Fe = N_2O + FeO.$$

Priestly first prepared the latter gas by this method.

The existence of gaseous nitrous anhydride, N_2O_3, is doubtful, there being strong reason to suppose that in all cases where chemists have endeavored to obtain pure nitrous anhydride they have only succeeded in producing a mixture of nitric oxide (NO) and nitrogen peroxide (NO_2), which, obviously, would contain the same proportion of nitrogen and oxygen by weight as would N_2O_3.

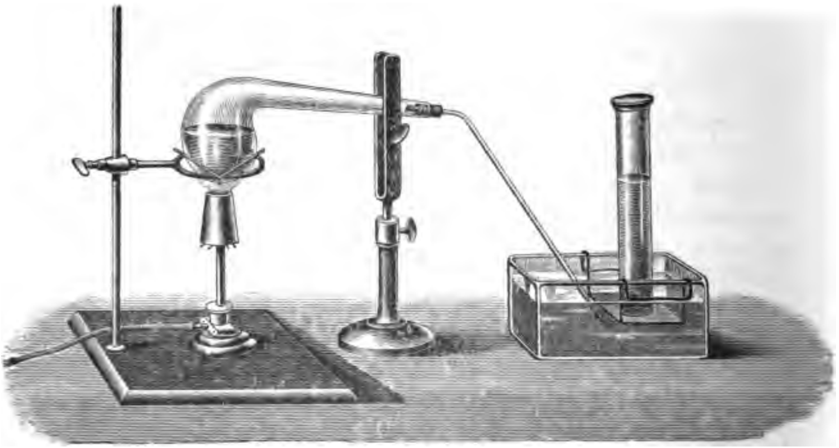

FIGURE 37.

$$NO + NO_2 = N_2O_3$$

The brown gas which results when nitric oxide is mixed with an excess of oxygen is nearly pure nitrogen peroxide (NO_2) but that which is formed by mixing nitric oxide with an amount of oxygen not sufficient to produce the peroxide, undoubtedly consists of a mixture of nitrogen dioxide and nitrogen trioxide. Both of these gases are easily condensed to the liquid form, in which state nitrogen trioxide apparently can exist. Fluid nitrogen trioxide is an indigo-colored liquid which is formed at —10° and which boils below 0°, giving off dark brown vapors which change, in part at least, into nitric oxide and nitrogen peroxide.

Nitrogen peroxide is produced when nitric oxide is exposed to the atmosphere:

$$NO + O = NO_2,$$

or by heating the nitrates of a number of metals, the most convenient nitrate for this purpose being that of lead.[55]

$$Pb\,(NO_3)_2 = Pb\,O + 2\,NO_2 + O^*$$

The gas has a dark brown color which deepens as the temperature is increased, it has a corroding action, giving a saffron coloring to the skin and other nitrogen-bearing organic compounds. A moderate cold condenses the gas to a yellow liquid, which becomes lighter in color the lower the temperature and which solidifies at —9° to —15° and boils at about 22°. Nitrogen peroxide, when a gas at a temperature just above the boiling point of the liquid, has a specific gravity which indicates that its molecule has the formula $N_2\,O_4$, but these molecules, as the temperature increases, begin to break down into those having the composition NO_2, so that the specific gravity of this substance diminishes until 140° is reached, when the dissociation of $N_2\,O_4$ into NO_2 is complete; at 600° the gas has become entirely colorless and has decomposed into nitric oxide and oxygen. Nitrogen peroxide is a powerful oxidizer; carbon and strongly heated phosphorus burn in it, and the presence of this gas dissolved in fuming nitric acid probably gives rise to the powerful oxidizing action of the latter substance. Nitrogen peroxide is changed into nitric acid and nitric oxide when it is dissolved in water, so that the same tendency to form the acids with the greatest possible amount of oxygen, which we saw in the halogene and sulphur families, is once more observed in the case of the compounds under discussion.

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*The nitrate of lead first, undoubtedly, breaks down into lead oxide and nitric anhydride,

$$Pb\,(NO_3)_2 = Pb\,O + N_2\,O_5,$$

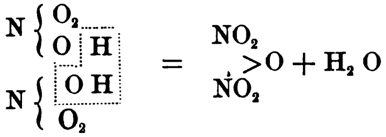
just as nitric acid would break down into water and nitric anhydride:

$$2\,H\,(NO_3) = H_2\,O + N_2\,O_5.$$

but the latter, at the temperature of the reaction, forms oxygen and nitrogen peroxide,

$$N_2\,O_5 = 2\,NO_2 + O.$$

Nitrogen pentoxide is the anhydride of nitric acid and is best prepared by removing the water from concentrated nitric acid by means of phosphoric anhydride:[56]



$$\begin{array}{l} N\left\{\begin{array}{l} O_2 \\ O\,H \end{array}\right. \\ N\left\{\begin{array}{l} O\,H \\ O_2 \end{array}\right. \end{array} = \begin{array}{l} NO_2 \\ NO_2 \end{array}\!\!>O + H_2\,O$$

$$2\,H\,NO_3 = N_2\,O_5 + H_2\,O.$$

The compound is a crystalline solid which melts at 30° and boils at 45.5°, while at the same time it is partially decomposed; it cannot be kept for any length of time because it breaks down into nitrogen peroxide and oxygen,

$$N_2\,O_5 = 2\,NO_2 + O.$$

Dangerous explosions may be the result of this decomposition if the pentoxide has been kept in a sealed tube. Nitric anhydride forms nitric acid when added to water.

$$N_2\,O_5 + H_2\,O = 2\,HNO_3.$$

Nitric acid has been known ever since the time of the Arabian alchemists. The first authentic account of its preparation is given by Geber, who, in the ninth century, made it by distilling a mixture of saltpetre (potassium nitrate), blue vitriol (copper sulphate) and alum (aluminium and potassium sulphate). The first samples of nitric acid were undoubtedly an impure article. The name given to it was *aqua dissolutiva* or *aqua fortis*, while *aqua regia* was used to designate a mixture of nitric and hydrochloric acids. Nitric acid, or *aqua fortis*, the alchemists discovered, had the power of dissolving all known metals with the exception of gold, while *aqua regia* would even attack this so-called noblest of all metals—almost nothing could withstand its corrosive action; surely, thought they, this liquid must be closely allied to the "alcahest," the universal solvent which they were seeking. At the beginning of the eighteenth century nitric acid was extensively made by the action of sulphuric acid on nitre (saltpetre); to this method of preparation it owes its present name, which is derived from *spiritus nitri*. Lavoisier first proved that nitric acid contained oxygen, and its definite composition was ascertained during the present century.

Nitric acid can be produced by the direct union of nitrogen, oxygen and water. Such a synthesis takes place when electric sparks are passed through moist air$_{57}$. In all probability nitrogen peroxide, NO_2, is at first generated,* however, the latter, when in contact with water, breaks down into nitric oxide and nitric acid. (See page 193). Oxides of nitrogen are also produced during combustion in the air;† these oxides, in contact with moisture, are further converted into nitric acid and, as ammonia is generally present in the air, this, uniting with the nitric acid, produces ammonium nitrate, so that the latter substance occurs in the atmosphere. Nitric and nitrous acids are, however, much more readily formed by the oxidation of ammonia or the oxides of nitrogen than by the direct union of the elements. When organic substances which contain nitrogen decay, the nitrogen passes off as ammonia which, with the acids present in the air and with the carbon dioxide formed at the same time, produces ammonium carbonate, nitrate and nitrite (page 165) but when bases are present in the soil, an oxidation of the nitrogen takes place so that nitrates are

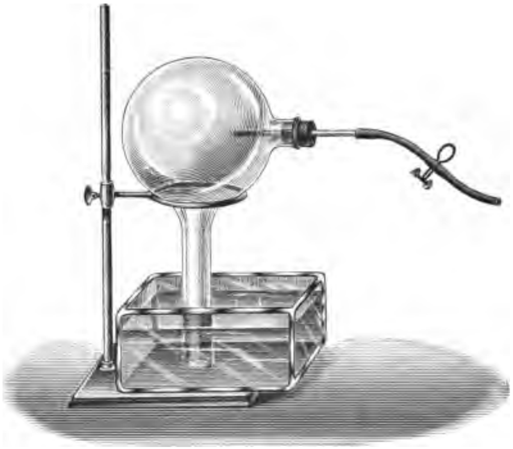


FIGURE 38.

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* This method for the preparation of nitrogen dioxide reminds us of the similar one used in forming ozone (see page 48). Nitrogen and oxygen are both the first members of their respective families, there is but little difference between their atomic weights and hence they should show points of resemblance, as indeed they do, for they are both colorless gases. Ozone can be considered as the oxide of oxygen, OO_2; it then corresponds to the oxides of sulphur, selenium and tellurium, SO_2, $Se O_2$ $Te O_2$. In the manner of its formation and in its formula it is analogous to nitrogen peroxide, NO_2; furthermore, being an endothermic compound, it has a great tendency to give up one atom of oxygen, $OO_2 = OO + O$, just as nitrogen peroxide does, $NO_2 = NO + O$.

† This formation takes place in greatest quantity when hydrogen is burned in air.

produced instead of these ammonium salts. Calcium nitrate is therefore frequently found on the walls of stables and cellars, while in the neighborhood of East Indian villages, where the surface soil contains potash, potassium nitrate is extensively met with; the collecting of this substance forms the exclusive occupation of a number of natives. Large deposits of sodium nitrate occur in the province of Tarapaca in the northern part of Chili, this substance is known as Chili saltpetre or nitre; its presence is probably due to the decay of marine vegetation which flourished on what is now terra firma, during the period when a portion of the South American coast was submerged. This supposition is sustained by the fact that sodium chloride and salts containing bromine and iodine are found mixed with the nitre.

Nitric acid is best prepared for laboratory use by the addition of sulphuric acid to a nitrate, a method which we have so often employed in the isolation of other acids, (see page 148). The reaction takes place as follows:

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3,$$

or, if comparatively little sulphuric acid is used:

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3,$$

for, when an excess of the salt is present the secondary, and not the primary sulphate results. (See page 149).[58]

Nitric acid is a colorless liquid which has probably never been prepared entirely free from water. It boils at 86° and becomes solid at —47°, if it contains water enough to have a specific weight of 1.3 it congeals at —19°, the purest acid known has a specific gravity of 1.55,* it fumes in the air and turns yellow when exposed to the sunlight, because it breaks down into nitrogen peroxide, water and oxygen. The same change takes place when nitric acid is distilled, for the distillate from a colorless, pure acid is colored because of decomposition. This behavior reminds us forcibly of the chlorine acids. At temperatures just above the boiling point of nitric acid the specific gravity of the vapor shows that but little decomposition has taken place, for the molecular weight of HNO_3 would be 63 and the specific gravity of the vapor, $H = 2$, is 59.3; the vapor density of the acid diminishes as the temperature is increased until at 250° it is 36, therefore, at that temperature, the following change has taken place;

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* The pupil must remember that the specific gravities of liquids and solids are taken with water as unity.

$$4\ HNO_3 = 2\ H_2O + 4\ NO_2 + O_2^*.$$

Considerable heat is evolved when nitric acid is dissolved in water, so that the dilute acid possesses less chemical energy and is therefore more stable than the concentrated one. It is doubtful if definite hydrated acids, such as were encountered with sulphuric acid, are derived from nitric acid, certainly the heat of solution of the latter† is much less than that of the former. (See pages 141, 147).

Nitric acid has a great tendency to give up its oxygen when brought in contact with reducing substances. Examples of this oxidizing effect we have seen in the preparation of sulphuric from sulphurous acid (page 143) and in the formation of nitric oxide from copper and nitric acid (page 190). Nitric acid will attack many organic substances in the same way, for it oxidizes them, while at the same time the acid itself is reduced; when the substance attacked is like starch or sugar, the oxides N_2O_3 and NO_2 are the main products. The organic substance is often completely burned, yet in

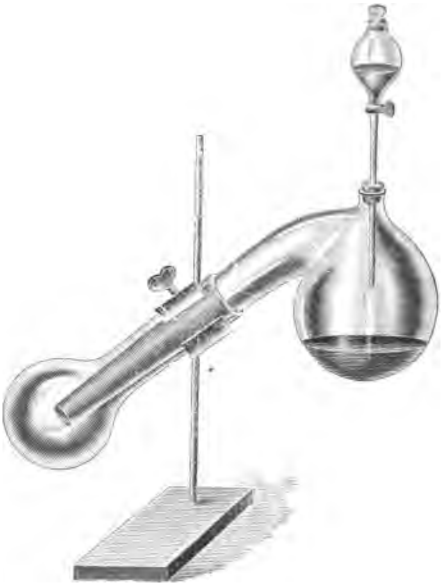

FIGURE 39.

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* If a volume of hydrogen weighs 2 grams then the same volume of nitric acid weighs 63 grams, 4 volumes of nitric acid would therefore weigh 252 grams. These decompose into 2 volumes of water vapor, weighing 36 grams, 4 of nitrogen peroxide weighing 184 grams and 1 of oxygen weighing 32 grams. The 4 volumes of nitric acid therefore yield 7 volumes of the decomposition products, these 7 volumes weigh 252 grams, 1 volume equal to that of 2 grams of hydrogen, therefore weighs 36 grams, in other words, provided this decomposition takes place, the specific gravity of the mixed gases must be 36, if H = 2. (See pages 67 and 183).

† 71 K.

quite a number of cases the body attacked is so **changed** that th nitro-group, NO_2 (see nitrosyl sulphuric acid, page 144, foot note) i substituted for hydrogen, such an action is produced when nitr acid attacks glycerine, forming nitro-glycerine. Concentrate nitric acid violently attacks the skin and mucous membrane, the portion with which it has come in contact turns yellow, blisters an finally forms an ulcer; if the acid is somewhat dilute the yellow color will appear without the blistering; it also attacks silk in th same way, turning it yellow and, if the acid is concentrated, destroy-ing it. The acid attacks vegetable dyes, so that cloth upon which nitric acid has accidentally been dropped cannot be restored to it original color by neutralization with ammonia water.[59]

As we have seen, many metals dissolve in nitric acid to form the corresponding nitrate, a reduction product being produced at the same time. These reactions can practically be classed under two heads.

a. Those in which ammonia is produced; the ammonia at once uniting with nitric acid to form ammonium nitrate; this change takes place when dilute nitric acid is added to zinc, tin or to some other metals, the reaction can be represented in three stages, as follows:

1. $8\ HNO_3 + 4\ Zn = 4\ Zn(NO_3)_2 + 8\ H$,—formation of hydrogen.

2. $HNO_3 + 8\,H = 3\,H_2O + NH_3$; $NH_3 + HNO_3 = NH_4\,NO_3$,– reduction of nitric acid and formation of ammonium nitrate,

3. $4\ Zn + 10\ HNO_3 = 4\ Zn\ (NO_3)_2 + NH_4\ NO_3 + 3\ H_2\ O$,– complete reaction.

b. Those in which nitric oxide is formed.

$3\,Cu + 8\,HNO_3 = 3\,Cu\ (NO_3)_2 + 2\,NO + 4\ H_2O$. (Page 190).

These two classes of reactions, however, only represent what most frequently takes place, it is known, for instance, that when zinc acts on a mixture of nitric and sulpuric acids, a partially oxidized ammonia known as hydroxylamine, $NH_2\ OH$, results and when copper is dissolved in nitric acid alone, nitrous oxide and even nitrogen are given off; the production of nitrous oxide increasing with the amount of copper nitrate present. In attempting to construct equations for such reactions we therefore generally represent only the *principal* changes which take place.

The reduction of nitric acid is generally attributed to the action of nascent hydrogen, and certainly the experimental proofs all seem to indicate that this theory is well founded. We cannot enter into the subject very deeply in this text-book,* but the following facts may not be out of place. When a piece of magnesium is dissolved in dilute nitric acid, hydrogen is at first given off; the production of hydrogen, however, soon ceases, while the oxides of nitrogen make their appearance; it also seems very probable that the hydrogen which has been occluded by palladium (page 32) passes through nitric acid unchanged *until that hydrogen which is supposed to be chemically combined* with the palladium begins to be liberated; then the evolution of hydrogen stops while the lower oxides of nitrogen make their appearance. Apparently, then hydrogen which is just in the act of being liberated from its compounds has a greater chemical activity than has ordinary hydrogen, so that, whether we regard this hydrogen as acting by reason of its existence as individual atoms or not, there is no reason why we should not consider the reduction of nitric acid by dissolving metals therein as being caused by hydrogen. The equations given above are intended to illustrate this conclusion.

Nitric acid is a monobasic acid, it has in its formula weight but one hydrogen atom which can be replaced by metals. The nitrates are all decomposed by heat, the change taking place in one of three ways:

a. The nitrate is entirely decomposed, as is ammonium nitrate (page 188).

β. The nitrate breaks down into the oxide of the metal, oxygen and nitrogen peroxide: $Pb\,(NO_3)_2 = Pb\,O + 2\,NO_2 + O$, (see page 193.) If the oxide of the metal is decomposed by heat, of course nothing but the metal remains.

γ. The nitrate gives off oxygen, leaving the nitrite. This decomposition is confined to the nitrates of very pronounced metals like potassium or sodium.

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*For a more complete account of nascent reactions the pupil can refer to M. M. Pattison Muir, "Principles of Chemistry."

In these decompositions nitrates differ from chlorates, for when the latter are heated the *perchlorates* are quite often produced, the reason is obvious, nitrogen cannot take up more oxygen than is necessary to form the oxide $N_2 O_5$, which is the anhydride of nitric acid (page 194), so that no pernitrates can be formed.

The existence of nitrous acid is doubtful, although the nitrites are stable and well characterized compounds. When an acid is added to a nitrite, the nitrous acid which is formed at once breaks down into its anhydride and water and the anhydride is further decomposed, so that NO_2 and NO are produced. By passing impure nitrogen trioxide, (formed by the reduction of nitric acid) into ice-cold water, a blue liquid, which possibly is nitrous acid, is produced, but the slightest increase in temperature causes the latter to change into nitric acid and nitric oxide.

FIGURE 40.

We have already studied the manner in which nitrites are formed by heating nitrates, so nothing more need be added excepting the statement that many nitrites can best be prepared from potassium nitrite by double decomposition (page 56), while that salt is produced by heating nitrate of potassium with lead.

The hyponitrites and hyponitrous acid alone remain for discussion.

The hyponitrite of potassium can be prepared by reducing nitrate of potassium with sodium amalgam (Ref. 32 of Appendix), the latter in contact with water forms sodium hydroxide and hydrogen, while hydrogen in the nascent state robs the potassium nitrate of its oxygen:

$$K\,NO_3 + 4\,H = K\,NO + 2\,H_2\,O.$$

The hyponitrite of silver, which is insoluble in water, can be prepared by adding silver nitrate to potassium hyponitrite,

$$Ag\,NO_3 + K\,NO = K\,NO_3 + Ag\,NO,$$

and the free acid can be formed from the latter by the addition of hydrochloric acid,

$$Ag\,NO + H\,Cl = Ag\,Cl + H\,NO.^{*}$$

Hyponitrous acid exists only in very dilute solutions, when warmed or when allowed to stand, it decomposes, yielding nitrous oxide (its anhydride) and water

$$2\,H\,NO = H_2\,O + N_2\,O.$$

The acid is of no practical importance.

In the following table the nitrogen compounds are compared with those of chlorine:

OXIDES.	ACIDS.	NAMES.	OXIDES.	ACIDS.	NAMES.
$Cl_2\,O$	$HO\ Cl$	Hypochlorous acid	$N_2\,O$	$H\,O\ N$‡	Hyponitrous acid
$Cl_2\,O_3$	$HO_2\,Cl$	Chlorous "	$N_2\,O_3$	$H\,O_2\,N$§	Nitrous "
$(Cl_2\,O_5)$†	$HO_3\,Cl$	Chloric "	$N_2\,O_5$	$H\,O_3\,N$	Nitric "
$(Cl_2\,O_7)$†	$HO_4\,Cl$	Perchloric "	——	——	——

† Oxides $Cl_2\,O_5$, $Cl_2\,O_7$ do not exist, the corresponding acids $HO_3\,Cl$, $HO_4\,Cl$, do.

‡ Hyponitrous acid breaks down into its anhydride, $N_2\,O$, and water, but cannot be formed by dissolving $N_2\,O$ in water.

§ Nitrous acid is only stable in very cold water. The existence of the anhydride $N_2\,O_3$ is doubtful.

The salts of these acids are much more stable than the acids themselves. All of the acids are powerful oxidizers, all of the oxides are unstable. Those of chlorine are explosive, those of nitrogen support conbustion.

$Cl\,O_2$ and NO_2 are not the anhydrides of acids. The former on addition of water forms *chloric* and *chlorous* acids, $Cl\,O_2 + H_2\,O = H\,Cl\,O_2 + H\,Cl\,O_3$, the latter *nitric* acid and *nitric oxide*, $3\,NO_2 + H_2\,O = 2\,H\,NO_3 + NO$. At low temperatures NO_2 becomes $N_2\,O_4$ and probably $Cl\,O_2$ becomes $Cl_2\,O_4$.

The acids are all unibasic.

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[*] Silver chloride is insoluble in water.

The heats of formation of the oxides of nitrogen, as far as they have been ascertained, are given in the following table:

$N_2\,O$ $N\,O$ $N\,O_2$ $N_2\,O_5$	—181 K —216 K — 77 K 131 K	Nitric oxide should be less stable than nitrous oxide, as a consequence NO is changed to N_2O by moist iron filings, zinc dust etc., NO_2 is more stable than NO, and is produced therefrom readily by the addition of oxygen. The higher oxides are more stable than those with less oxygen. N_2O_5 is an exothermic compound; it is a crystalline solid which can easily be formed from nitric acid by extracting water.
$H\,NO_2$ $H\,NO_3$	308 K* 491 K*	Nitric acid has a greater heat of formation than has nitrous acid; it is therefore the acid of oxygen and nitrogen which is most easily formed. The same rule is observed in the halogene and oxygen families, where those acids which contained the most oxygen are the most stable.

* Acids in solution.

CHAPTER XXVIII.

PHOSPHORUS AND PHOSPHINE.

Phosphorus, symbol P, atomic weight 31, specific gravity of yellow phosphorus 1.83, of red phosphorus 2.1. Specific gravity of vapor, air = 1 is 4.16, H = 2 is 119.80; molecular weight 124, molecule P_4. Phosphine, formula PH_3, specific weight, air = 1 is 1.176, H = 2 is 33.86; molecular weight 34, 1 c. c. of the gas at 0° and .76 M weighs .0015276 grams.

Phosphorus never occurs as such in nature, indeed, such a possibility is precluded by the chemical nature of the element, as an example of which we have but to recall the energy with which it burns in oxygen. The compounds of phosphorus which are most frequently found are:

Apatite, a combination of calcium phosphate and calcium chloride (or fluoride), $Ca_3(PO_4)_2 . CaCl_2$,

Phosphorite, calcium phosphate, $Ca_3(PO_4)_2$,

Vivianite, ferrous phosphate, $Fe_3(PO_4)_2 + 8 H_2O$, as well as phosphates of aluminum and lead.

Phosphates are always present in the soil; they are essential to the growth of plants and are taken up by the roots, so that plant ashes, especially those of the cereals, often contain large quantities of the phosphates of calcium and magnesium; the later find their way into the animal organism where calcium phosphate forms a large part of the bones, the waste products are returned to the soil in the solid excrements and in the urine, so that, as manure, they are once more brought into the proper condition to play their part in plant growth. These changes taking place with phosphoric acid remind us forcibly of the similar ones encountered with carbon dioxide and ammonia, none of these necessary substances are the permanent property of any one organism, they are simply borrowed for a time, and must be returned to the place from which they came.

Phosphorus was discovered by a Hamburg alchemist named Brand, who accidentally prepared the element while searching for the philosopher's stone. Subsequently Kunkel published an account describing a method of obtaining the substance, but until the middle of the last century the supply was so small that phosphorus was a very expensive article; it was exclusively prepared from decaying urine and the price in England was ten ducats an ounce. At a later date a method was discovered by which phosphorus could be obtained from the calcium phosphate procured either from the mineral phosphorite or from bones, but even then it was mainly kept as a curiosity until the introduction of matches rendered its cheap production necessary. At the present time phosphorus is prepared from bones by first burning the latter in order to destroy the organic matter contained in them, the calcium phosphate is then changed to the primary phosphate of calcium ($Ca (H_2 PO_4)_2$) by means of sulphuric acid. Primary phosphates are soluble in water, so that a solution can be formed which is further evaporated and heated, by which means the primary phosphate of calcium loses water and is converted into calcium metaphosphate ($Ca (PO_3)_2$); and the latter substance, when heated with charcoal and sand, yields phosphorus.

Phosphorus exists in two allotropic forms,* the most common of which is a slightly yellow, wax-like solid which becomes brittle when cold and which is readily soluble in carbon bisulphide; it melts at 44° and boils at 290°, forming a colorless vapor which has a specific gravity of 4.16 at red heat. This, with hydrogen as two, gives 119.8, while the molecular weight of P_4 would be 124. The observed specific gravity is therefore somewhat less than the molecular weight 124, a fact which probably finds its explanation in the decomposition of some of these complex molecules into simpler ones. At white heat the specific gravity of phosphorus vapor has diminished to 3.0, so that at this temperature nearly all of the P_4 molecules have dissociated into those having the composition P_2.

When a solution of ordinary phosphorus in carbon bisulphide is exposed to the sunlight, the other, insoluble, red, amorphous modification of the element gradually separates. This change can be accomplished more quickly and effectually by heating phosphorus to about 300° in a closed vessel;[60] the same transformation also occurs through the influence of electricity. Amorphous phosphorus is a dark red substance, which is generally produced in the form of a powder the specific gravity of which is 2.1. When heated to 261° under atmosphoric pressure in hydrogen or carbon dioxide, amorphous phosphorus is changed back to the yellow variety; the kindling temperature of the former about coincides with this point. The transformation of the element from its ordinary crystalline form into the amorphous one is only accomplished when the phosphorus is under a pressure of several atmospheres and at a higher temperature.

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* A form of phosphorus resembling flowers of sulphur has been prepared by rapidly cooling phosphorus vapors. This may be a third allotropic form of phosphorus.

Red phosphorus is perfectly insoluble in carbon bisulphide, ether and similar substances by which the other allotropic form is readily dissolved. It can be exposed to the atmosphere for any length of time without change, while the other variety will absorb oxygen, melt and, under proper conditions, may take fire spontaneously. Yellow phosphorus, when placed in warm, moist air and in the dark, emits a pale white light* which is in part due to the slow oxidation of the element.†

Yellow phosphorus is an intense poison, even small doses cause local inflammations in various organs of the body and have a secondary effect on the nervous system. The serious symptoms caused by poisoning with phosphorus only become apparent some hours after taking, they manifest themselves by intense pain in the gastric region, finally extending throughout the entire abdomen; the vomit will contain phosphorus, have a peculiarly garlic-like odor and will be luminous in the dark, the patient is restless, fearful and trembling. The post-mortem examination reveals inflammation of the mucous membrane of the stomach, accompanied by fatty degeneration of the liver, kidney and heart. Fatal doses are from .2 to .5 grams. Cases of phosphorus poisoning are not uncommon, as phosphorus mixed in a dough made of cold water and flour is frequently used as a rat-poison, this has especially been the case since the element has become quite cheap by reason of its use in the manufacture of matches, the heads of a number of varieties of which are made of a mixture of gum arabic and phosphorus.

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* So called phosphorescence.

† That this is not entirely so is proven by the fact that phosporus is not luminous in dry oxygen below 20° C, or in that gas under pressure.

Yellow phosphorus is soluble in carbon bisulphide, ether and etherial oils, it is insoluble in alcohol and water, but volatile in the vapors of the latter. When slowly oxidized in moist air it changes to phosphorous acid:

$$2\,P + 3\,O = P_2O_3,$$
$$P_2O_3 + 3\,H_2O = 2\,PO_3H_3,$$

this change is supposed to be the cause of the phosphorescence of the element. When burned, both yellow and red phosphorus yield phosphorus pentoxide, which can further unite with water to form phosphoric acid.

$$2\,P + 5\,O = P_2O_5,$$
$$P_2O_5 + 3\,H_2O = 2\,PO_4H_3.$$

The element will combine with chlorine, bromine or any of the halogenes, just as it will with oxygen. (See page 61). Both of the oxides of phosphorus are anhydrides and all of the halogene compounds are decomposed by water. (See pages 77, 81).

Phosphorus forms three compounds with hydrogen, PH_3, phosphine, P_2H_4 liquid hydrogen phosphide and P_4H_2, solid hydrogen phosphide.

Phosphine is a gas which bears the same resemblance to ammonia that hydrogen sulphide does to water. As ammonia was formed with difficulty by the direct union of nitrogen and hydrogen, we would scarcely expect phosphine to be produced in a similar way, and yet the compound seems to be readily procured as a result of the action of nascent hydrogen upon phosphorus.* This unexpected result is possibly due to the fact that the breaking stress of the molecules of phosphorus is less than the same for those of nitrogen. The best method of preparing phosphine for laboratory use is by decomposing calcium phosphide with water or dilute acids. The formula of calcium phosphide has not been definitely ascertained, but we can compare this reaction with similar ones in which hydrochloric acid or hydrogen sulphide have been produced by the action of an acid upon a chloride or a sulphide. Another way, which has less to recommend it, but which is more frequently used, is by heating small pieces of phosphorus in a solution of potassium hydroxide.[61][*]

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* By throwing small pieces of phosphorus into a flask in which zinc and dilute sulphuric acid or tin and sulphuric acid are generating hydrogen, the temperature being about 70°. Compare J. Brössler, Berichte der Deutschen Chemischen Gesellschaft, 1881, 1757.

The gas formed by either of these methods is a mixture of PH_3 and P_2H_4, (unless concentrated hydrochloric acid was used to decompose the calcium phosphide). This mixture spontaneously takes fire in the air, while pure phosphine, PH_3, does not possess this property. The spontaneously inflammable gas can be altered in this respect by passing it through a tube cooled with snow and salt, for by this means the liquid hydrogen phosphide is condensed, while the phosphine passes on, to be used as occasion requires.

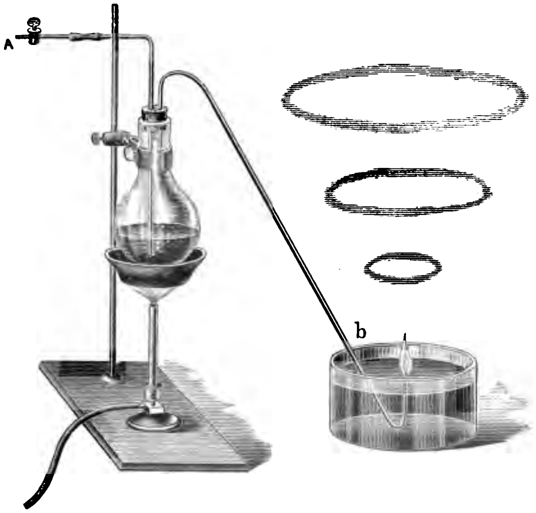

FIGURE 41.

Phosphine is a colorless gas with an intensely disagreeable, garlic-like odor. Its specific gravity, air=1, is 1.176, which, H=2, is 33.86. The molecular weight of PH_3 is therefore 34.021, for analysis has proven that in phosphine there are 31 parts of phosphorus and 3.021 of hydrogen by weight. It follows that 31 represents the maximum

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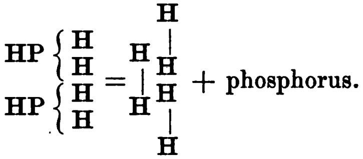
[*] The reaction is said to take place as follows:

$$3KOH + 4P + 3H_2O = 3KH_2PO_2 + PH_3.$$

The primary hypophosphite of potassium ($KPO + H_2O$) would thus be formed. The phosphine generated always contains hydrogen so that its formation is probably due to that element acting in the nascent state.

value for the atomic weight of phosphorus, for, as the molecular weight of phosphine is known, we cannot imagine any atomic weight for phosphorus greater than this number without believing that we have a fraction of an atom of that element in PH_3. When phosphine is heated, or when electric sparks are passed through it, the gas breaks down into phosphorus and hydrogen; in this case two volumes of hydrogen phosphide yield three of hydrogen, the phosphorus, being solid, when separated exerts no influence on the volume of the gas as a whole. (Compare pages 94 and 134).



$$\begin{array}{l}\mathrm{HP}\left\{\begin{array}{l}\mathrm{H}\\\mathrm{H}\end{array}\right.\\\mathrm{HP}\left\{\begin{array}{l}\mathrm{H}\\\mathrm{H}\end{array}\right.\end{array} = \begin{array}{c}\mathrm{H}\\|\\\mathrm{H}\end{array}\;\begin{array}{c}\mathrm{H}\\|\\\mathrm{H}\\\mathrm{H}\\|\\\mathrm{H}\end{array} + \text{phosphorus.}$$

From this equation it is evident that two molecules of phosphine produce three of hydrogen, but the terms "volume" and "molecule" can be used interchangeably, as we saw on page 67.

Phosphine can be mixed with pure oxygen without taking fire, but if the pressure is suddenly diminished the gases will explode. In the air the kindling temperature is 149°,* the products of the combustion are phosphoric anhydride and water:

$$2\,PH_3 + 8\,O = P_2\,O_5 + 3\,H_2\,O,$$

but these two substances naturally combine to form phosphoric acid:

$$P_2\,O_5 + 3\,H_2\,O = 2\,H_3\,PO_4.$$

Of course chlorine, bromine or iodine would act on phosphine in exactly the same way,† the products being the respective halhydric acids and the corresponding halogene compounds of phosphorus:

$$PH_3 + 6\,Cl = P\,Cl_3 + 3\,H\,Cl.$$

So readily is phosphine decomposed that even sulphur, when placed in contact with that substance, changes it to the sulphide of phosphorus and hydrogen sulphide, so that here we have an instance in which sulphur causes changes similar to those produced by oxygen and the halogenes. It need scarcely be added that concentrated sulphuric or nitric acid will decompose phosphine just as they would hydrobromic acid, hydoiodic acid or sulphuretted hydrogen. When phosphine is passed into solutions of metallic salts it, in many cases, produces the corresponding phosphides of the metals (compare sulphuretted hydrogen, page 95). Phosphine is sparingly soluble in water, and is very poisonous, so that all operations in which it is generated must be conducted either in the open air or under a hood with a strong draught. The gas changes to a liquid at —85° and becomes solid at —133°.

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* The friction of the glass-stopper in the neck of a bottle filled with phosphine may be sufficient to ignite the gas.

† Chlorine and phosphine, when mixed, explode very violently.

Phosphine can unite with the halhydric acids to form phosphonium compounds exactly as ammonia does in the production of ammonium salts, the group PH_4 being called phosphonium for the same reason that NH_4 is ammonium.

$$PH_3 + HI = PH_4I, \text{ phosphonium iodide,}$$
$$NH_3 + HI = NH_4I, \text{ ammonium iodide.}$$

As phosphine is readily oxidized and is much less basic in its character than is ammonia* it will not unite with acids containing oxygen, in this respect it differs from ammonia. The phosphonium compounds are readily decomposed by water or by alkalis.

$$PH_4I + H_2O = PH_3 + HI + H_2O,$$
$$PH_4I + KOH = PH_3 + KI + H_2O,$$

the latter reaction being exactly like those observed with ammonium salts:

$$NH_4I + KOH = NH_3 + KI + H_2O.$$

It follows that phosphonium salts cannot be formed where water is present.

The compound P_2H_4 is a liquid at ordinary temperatures. It is formed, as was stated above, by cooling the mixture of gases obtained by one of the ordinary methods in use for the production of phosphine. It is a colorless, highly refractive liquid which boils at about 35°, and which takes fire spontaneously when exposed to the air. The determination of the specific gravity of the vapor shows it to have a molecular weight of 66, its formula is therefore $PH_2 — PH_2$; the analogous compound of nitrogen is hydrazine, $NH_2 — NH_2$, but, unlike the latter, liquid hydrogen phosphide is not basic and can therefore form no salts. This fact is not surprising if the same diminution of basic properties takes place with the hydrogen compounds of phosphorus as was observed in the case of the similar ones containing nitrogen. (Page 146, foot note).

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* See page 172.

The solid compound $P_4 H_2$ is formed by treating phosphine with chlorine which has been highly diluted with carbon dioxide by which means a part of the hydrogen of phosphine is removed. It is a yellow powder which, when dry, can be heated as high as 150° without taking fire.

The following table shows the relationship between the compounds just discussed and the corresponding ones containing nitrogen:

NH_3, ammonia,	PH_3 Phosphine.	$NH_3 + HX = NH_4X$. Ammonium salts.
$N_2 H_4$, hydrazine,	$P_2 H_4$ liquid by Hydrogen Phosphide.	$PH_3 + HX = PH_4X$, Phosphonium salts.
$N_3 H$, azoimide,	....	Phosphonium fluoride has not, as yet, been prepared, with this exception X represents any halogene.
....	$P_4 H_2$ solid Hydrogen Phosphide.	

The compounds of nitrogen are all gases, they are not spontaneously inflammable, while those of phosphorus are either gaseous, liquid or solid and burn with the greatest ease.

CHAPTER XXIX.

THE COMPOUNDS OF PHOSPHORUS WITH THE HALOGENES AND WITH OXYGEN AND THE HALOGENES.

As the atomic weights in this family increase, an increasing stability of the compounds formed with the halogenes is observed. Those of nitrogen are very explosive substances, but in the case of the element under consideration a number of quite stable chlorides, bromides and iodides have been accurately studied, indeed, some of these can be classed among our most important laboratory reagents. They are given in the following table:

Fluorides.	Chlorides.	Bromides.	Iodides.
PF_3, phosphorus trifluoride,	PCl_3, trichloride,	PBr_3, tribromide,	PI_3, triodide
PF_5, phosphorus pentafluoride,	PCl_5, pentachloride,	PBr_5, pentabromide,	....

An iodide of Phosphorus P_2I_4, phosphorus di-iodide, exists.

The above compounds are all substances which, being the halogene compounds of a not metal, are readily decomposed by water to form the corresponding acid of phosphorus together with the hydrogen compound of the halogene which was used. We have seen that this instability in the presence of water has been made use of in the preparation of hydrobromic and hydroiodic acids. (Pages 77 and 81.)

The character of the trihalogene compounds changes somewhat with the nature of the halogene, the boiling point increases with the increase of the atomic weight just as it does in the case of the free elements, while the readiness with which these substances are decomposed is also, apparently, greater in the bromide and iodide than it is in the fluoride and chloride.

PF_3 is a gas, liquid at—10° under a pressure of 40 atmospheres.
PCl_3 is a liquid which boils at 74° heat of formation 755 K.
PBr_3 is a liquid which boils at 175° heat of formation 448 K.
PI_3 is a solid which melts at 55° and is decomposed by boiling.

PF_3, specific gravity of vapor, air = 1 is 3.02 which H = 2 is 87 the molecular weight is 88.

PCl_3, specific gravity of vapor, air = 1 is 4.8 which H = 2 is 138 the molecular weight is 137.5.

PBr_3, specific gravity of vapor, air = 1 is 9.7059 which H = 2 is 279.5 the molecular weight is 271.

From these determinations of the specific gravity of the vapors it is evident that the general formula of all of the trihalogene phosphides is PX_3 and that phosphorus is trivalent in these compounds just as it is in phosphine or just as nitrogen is in ammonia. The trihalogene phosphides are all formed by treating phosphorus with an amount of halogene insufficient to produce the compounds PX_5* and when they are decomposed by water they break down as follows:

$$P\left\{\begin{array}{l} X + HOH \\ X + HOH \\ X + HOH \end{array}\right. = P\left\{\begin{array}{l} OH \\ OH \\ OH \end{array}\right. + 3\,H\,X,$$

so that phosphorous acid results in all cases.

Phosphorus is unsaturated in the trihalogene compounds and is therefore capable of a further addition to form pentahaloids, the valence of the element increasing from three to five:

$$P\,X_3 + 2\,X = P\,X_5.$$

PF_5 is a gas which liquifies at 16°, 46 atmospheres pressure.

PCl_5 is a solid that boils at about 160°.

PBr_5 is a solid which decomposes into bromine and phosphorus tribromide at 100°.

These compounds, when added to water, yield *phosphoric* acid,

$$P\left\{\begin{array}{l} X + HOH \\ X + HOH \\ X + HOH \\ X + HOH \\ X + HOH \end{array}\right. = P\left\{\begin{array}{l} -O-H \\ -O-H \\ -O-H \\ -O-H \\ -O-H \end{array}\right. + 5\,HX.$$

From the above equation we would expect the production of *normal* phosphoric acid, but, as we have already seen, the normal acids have the greatest tendency to separate water, by this means yielding more stable compounds (pages 126 and 127) so that $P\,(O\,H)_5$ breaks down to form ordinary phosphoric acid:

$$P\,(O\,H)_5 = P\,O_4\,H_3 + H_2\,O.$$

The difference between the tri and pentachloride of phosphorus lies in the different amounts of chlorine contained in each; in the one phosphorus is trivalent, in the other it is quinquivalent, the one yields phosphorous acid, the other phosphoric acid by the addition of water, so that plainly the same difference in the valence of phosphorus exists in the acids as was found in the chlorides. Compounds containing both bromine and chlorine can be formed by adding bromine to the trichloride or chlorine to the tribromide of phosphorus. Under proper conditions a portion of the chlorine or bromine in the pentachloride or bromide of phosphorus can be replaced by oxygen; the result is an oxychloride or bromide of phosphorus with a chemical character analogous to the similar sulphur compounds discussed on page 152.

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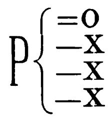
* Excepting the trifluoride which is formed by a somewhat complicated process.

$POCl_3$—phosphorus oxychloride, liquid, boils at 110°.
$POBr_3$—phosphorus oxybromide, solid, melts at 55° and boils at 193°.

These substances are produced by adding a small amount of water to the pentachloride or bromide of phosphorus:

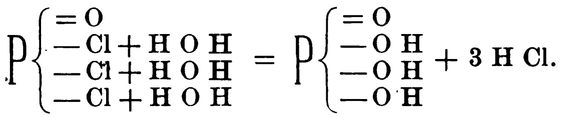
$$PX_5 + H_2O = POX_3 + 2\,HX.$$

In effecting this change one atom of oxygen has taken the place of two atoms of chlorine or bromine, so that the constitution of these compounds is as follows:



$$P\left\{\begin{array}{l} =O \\ -X \\ -X \\ -X \end{array}\right.$$

Phosphorus oxychloride or bromide are converted into ordinary phosphoric acid by the addition of water, therefore the latter compound contains three hydroxyle groups and is formed as follows:



$$P\left\{\begin{array}{l} =O \\ -Cl + HOH \\ -Cl + HOH \\ -Cl + HOH \end{array}\right. = P\left\{\begin{array}{l} =O \\ -OH \\ -OH \\ -OH \end{array}\right. + 3\,HCl.$$

All of the halogene compounds of phosphorus fume in the air, because moisture decomposes them while liberating hydrogen chloride, bromide or iodide. Phosphorus oxychloride and oxybromide have an indescribably unpleasant smell and all work with these substances, as well as with the pentahalogene compounds must be so conducted that the vapors cannot be inhaled.

CHAPTER XXX.

THE COMPOUNDS OF PHOSPHORUS WITH OXYGEN AND WITH OXYGEN AND HYDROGEN.

Phosphorus forms three oxides; two, $P_2 O_3$ and $P_2 O_5$, correspond to nitrogen trioxide, $N_2 O_3$, and nitrogen pentoxide, $N_2 O_5$, and one, $P_2 O_4$, is analogous to $N_2 O_4$. Some other oxides of phosphorus have been described, but further investigation must establish their identity. Phosphorus trioxide and pentoxide are both acidic anhydrides, the one of phosphorous, the other of phosphoric acid. The most common forms of these acids differ from the corresponding ones of nitrogen by being hydrated, so that phosphorous acid is not $H PO_2$ but $H_3 PO_3$, and phosphoric acid not $H PO_3$ but $H_3 PO_4$.

$P_2 O_3$, phosphorus trioxide, is produced by slowly oxidizing phosphorus in a stream of oxygen diluted with carbon dioxide. It is a crystalline solid which melts at 22.5° and which boils at 173.3°, being changed to a colorless vapor which has a specific gravity, air $= 1$, of 7.6, this indicates a molecule of the formula $P_4 O_6$, as the specific gravity calculated for $P_2 O_3$ is 3.8. The oxide is completely decomposed when heated to 300°, when phosphorus and the oxide $P_2 O_4$ are produced. Phosphorus trioxide is oxidized when brought in contact with oxygen, the action may even become so violent as to cause spontaneous combustion to ensue;* the oxidation product is phosphorus pentoxide. The latter substance, as we have seen, is also produced when phosphorus is burned in air or oxygen (page 20).[62] Ordinarily it is a flaky, not crystalline powder, however, it has been obtained in a crystalline form. Phosphorus pentoxide greedily absorbs moisture from the air; it is therefore deliquescent. The tendency to unite with water which is possessed by this substance is so great that if a little of it is placed in that liquid it dissolves with a hissing noise similar to that which is heard when a red-hot iron is immersed. Phosphoric anhydride, because it is able to perfectly absorb all moisture, is a favorite substance for drying gases, this desirable quality of completely removing all water is not possessed by the usual drying agent, calcium chloride.* Phosphorus pentoxide is quite volatile at 250°, but above that temperature it changes into another, so-called polymeric †, form which evaporates very slowly below bright red heat.

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*This phenomenon is possibly due to the fact that a mixture of $P_2 O_3$, $P_2 O_5$ and phosphorus is present after slow oxidation of phosphorus, the phosphorus would then cause the spontaneous combustion of the mass. Pure $P_2 O_3$ unites with oxygen and becomes luminous when placed in the gas under diminished pressure; the glowing ceases when the pressure is increased. This fact reminds us of the similar one observed with phosphorus and oxygen.

Phosphorous acid is produced when the trioxide or trichloride is dissolved in water; it is analogous to nitrous acid, although much more stable. When phosphorus trioxide unites with water the first product which we would expect would be $H\,PO_2$ for:

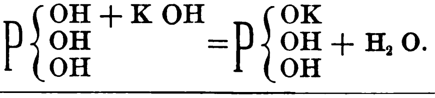
$$P_2\,O_3 + H_2\,O = 2\,H\,PO_2 \text{ (see page 110).}$$

The compound so produced, however, takes up one more molecule of water to form the hydrated acid $H_3\,PO_3$:

$$H\,PO_2 + H_2\,O = H_3\,PO_3,$$

in which condition, only, the acid is capable of existence.

Phosphorous acid contains three hydrogen atoms, but no more than two of these can be replaced by metals at the same time. The following explanation of this phenomenon seems the most reasonable. The character of any chemical compound is influenced by all of the elements in that compound; no one element or group of elements is able to entirely suppress any one of the others with which it is united. When a hydroxide (for instance that of potassium) reacts upon phosphorous acid it is to be presumed that the first product will be the primary salt; (page 137)



$$P\begin{cases}OH + K\,OH\\ OH\\ OH\end{cases} = P\begin{cases}OK\\ OH + H_2\,O.\\ OH\end{cases}$$

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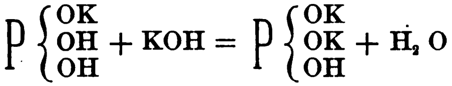
*It has been shown that a glass tube four inches in length, filled with phosphorus pentoxide will entirely dry a gas which is slowly passing through.

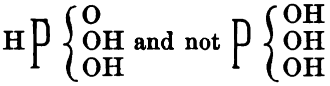
†The polymeric form of a substance is supposed to be produced by the union of simpler molecules of that substance to form a more complicated molecule. Thus, ordinary $P_2\,O_5$, let us suppose, is formed of molecules each of which is composed of x times the formula weight $P_2\,O_5$, or x ($P_2\,O_5$), each molecule of the polymeric form would then contain a number of these simpler molecules or *n* (x [$P_2\,O_5$])). Such polymeric forms are quite frequently met with in organic chemistry and possibly the phenomenon of allotropism may be caused by a union of simpler molecules to form more complex ones.

The metallic element which is now present in the salt renders the whole compound less negative, so that that the next reaction:



$$P\begin{cases}OK\\OH\\OH\end{cases} + KOH = P\begin{cases}OK\\OK\\OH\end{cases} + H_2O$$

would take place less readily than the first. The secondary salt has now entirely lost all acid properties, owing to the increased mass of metal present, so that all attempts to replace the third hydrogen atom will fail.* Many chemists think that experimental evidence has proven the formula of phosphorous acid to be:



$$HP\begin{cases}O\\OH\\OH\end{cases} \text{ and not } P\begin{cases}OH\\OH\\OH\end{cases}$$

so that it would contain only two hydroxyle groups. One of the hydrogen atoms would then be joined to phosphorus, thus rendering that element quinquivalent; by means of this hypothesis they have sought to explain the fact that phosphorous acid will only form primary and secondary salts. The remarks on page 153 will apply equally well in this case.

Phosphorous acid, like sulphurous and nitrous acid, is easily oxidized and when so acted on it forms phosphoric acid; chlorine, bromine, iodine, nitric acid and even sulphurous acid can affect it in this way. The following equations will serve as illustrations (see page 136):

a. $2\,Cl + H_2O = 2\,HCl + O$

b. $H_3PO_3 + O = H_3PO_4$,

Combining *a* and *b* we have:

c. $H_3PO_3 + 2\,Cl + H_2O = H_3PO_4 + 2\,HCl$.†

Phosphorous acid follows out the general rule which we observed with the chlorine and sulphur acids, it changes into the acid with greater amount of oxygen when heated. The change can be represented by the following equation:

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* A number of polybasic acids which are encountered in organic chemistry show this same character, they present the phenomenon of having one atom of the metal in their salts more reactive than the others.

† The pupil should practice the writing of a large number of equations in which cases of oxidation and reduction occur. In all case he must consider; first the substance to be oxidized; second, the amount of oxygen which it will take up; third, the oxidizing agent; and fourth, the amount of oxygen which the latter will yield and the products which it forms when it oxidizes. Examples of oxidation have been frequently given on the previous pages of this book.

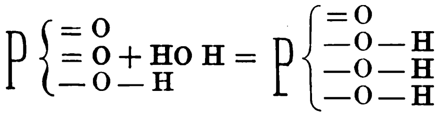
$$4\,H_3PO_3 = 3\,H_3PO_4 + PH_3.$$

The evolution of phosphine, if the phosphorous acid is heated too rapidly, can sometimes become so violent that an explosion takes place. Phosphorous acid is a colorless, crystalline solid which melts at 70°, and which is very soluble in water.

When phosphoric anhydride is exposed to the air it deliquesces and is converted into a phosphoric acid, which, however, is not the one usually encountered, but is the less hydrated acid corresponding to nitric or chloric acid; the following will make the parallelism clear:

$$\begin{array}{cccccc} P_2O_5 & + & H_2O & = & 2\,HPO_3, \\ \text{Phosphoric anhydride} & + & \text{Water} & = & \text{Phosphoric acid,} \\ N_2O_5 & + & H_2O & = & 2\,HNO_3, \\ \text{Nitric anhydride} & + & \text{Water} & = & \text{Nitric acid,} \\ Cl_2O_5 & + & H_2O & = & 2\,HClO_3, \\ \text{Chloric anhydride} & + & \text{Water} & = & \text{Chloric acid.} \end{array}$$

When the phosphoric acid so obtained is dissolved in an excess of water and allowed to stand for some time, or when it is boiled with water, it takes up more of that substance to produce the ordinary form of the acid; one oxygen atom together with the elements of water forming two hydroxyle groups:



$$P\begin{cases} =O \\ =O \\ -O-H \end{cases} + HOH = P\begin{cases} =O \\ -O-H \\ -O-H \\ -O-H \end{cases}$$

$$HPO_3 + H_2O = H_3PO_4.$$

The acid with the formula HPO_3 is called metaphosphoric, while H_3PO_4 has the name of orthophosphoric acid. Nitric acid, HNO_3, and chloric acid, $HClO_3$ are therefore really *meta* nitric and *meta* chloric acids, but as the corresponding *ortho* acids, H_3NO_4 and H_3ClO_4 are not known, there is no necessity of applying a special designation to the less hydrated and common form of these substances. The nomenclature which is applied to the acids derived from the other elements of this family corresponds to that used with phosphorus, thus:

$H\ As\ O_2$ is meta arsenious acid.
$H_3\ As\ O_3$ " ortho " "
$H\ As\ O_3$ " meta arsenic "
$H_3\ As\ O_4$ " ortho " "

and the same system is also frequently applied in the designation of acids derived from elements belonging to other groups, for instance:

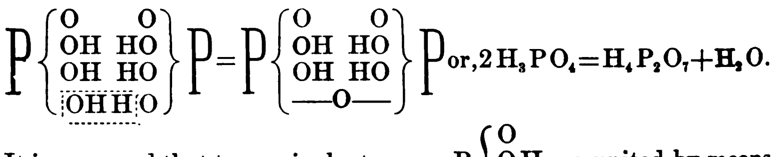
$H_2\ Si\ O_3$ is meta silicic acid,
$H_4\ Si\ O_4$ is ortho " "

Unfortunately this system is not rigidly carried out with all of the various hydrated acids which have been discovered and, furthermore, acids have been distinguished as ortho and meta when the difference between them has nothing whatever to do with their hydration, so that these distinctive names can only be used in cases where they have the sanction of custom.

Orthophosphoric acid changes into metaphosphoric acid at a red heat, and if this temperature is maintained for a sufficient length of time the latter substance will finally evaporate. When orthophosphoric is changed into metaphosphoric acid, a third acid is first produced as an intermediary product and this one, having its place between the other two acids is, because produced by heating, called pyrophosphoric acid. The changes which orthophosphoric acid undergoes can be represented by the following:

$$\underset{\text{Orthophosphoric acid.}}{2\ H_3\ PO_4} = \underset{\text{Pyrophosphoric acid.}}{H_4\ P_2\ O_7} + H_2\ O;\ \text{and}\ \underset{\text{Pyrophosphoric acid.}}{H_4\ P_2\ O_7} = \underset{\text{Metaphosphoric acid.}}{2\ H\ PO_3} + H_2\ O.$$

The structural formulæ representing the formation of pryophosphoric acid are as follows:



$$P\left\{\begin{matrix}O & O\\ OH & HO\\ OH & HO\\ \underline{OH\ H\vdots O}\end{matrix}\right\}P = P\left\{\begin{matrix}O & O\\ OH & HO\\ OH & HO\\ \multicolumn{2}{c}{—O—}\end{matrix}\right\}P\ \text{or,}\ 2\,H_3PO_4 = H_4P_2O_7 + H_2O.$$

It is supposed that two univalent groups $P\left\{\begin{matrix}O\\ OH\\ OH\end{matrix}\right.$ are united by means of oxygen, just as are two similar ones in disulphuric acid as was described on page 150; such complicated acids, produced by the separation of water and the joining of groups of elements by oxygen atoms are of quite frequent occurence.*

Metaphosphoric acid is a colorless, glass-like substance (*acidum phosphoricum glaciale*) which greedily absorbs moisture from the air. It is a monobasic acid and should therefore only form one class of salts, however, a number of metaphosphates derived from the same metal are known, the form of acid known as metaphosphoric acid is therefore supposed to be capable of existing in several polymeric forms†. Metaphosphoric acid precipitates egg albumen from its solutions, a property which distinguishes it from ortho and pyrophosphoric acid. Metaphosphoric acid changes to orthophosphoric acid on being dissolved in water and standing, it is rapidly converted by boiling the solution.

Orthophosphoric acid is tribasic, it forms primary, secondary and tertiary salts. Representatives of each of these classes are known and of importance. If M represents any *univalent* metal then:

$M H_2 PO_4$ is the primary phosphate,
$M_2 HPO_4$ is the secondary phosphate, and
$M_3 PO_4$ is the tertiary phosphate;

and if M′ is any *bivalent* metal then:

$M' (H_2 PO_4)_2$ is the primary phosphate,
$M' (H PO_4)$ is the secondary phosphate, and
$M'_3 (PO_4)_2$ is the tertiary phosphate.

The formulæ of the last three salts are self-evident if we consider that a bivalent metal replaces two hydrogen atoms of an acid and that a primary salt has one, a secondary two and a tertiary three

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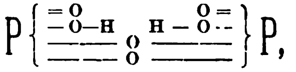
*From its formation by heating pyrophosphoric acid, it seems likely that ordinary metaphosphoric acid has the formula



$$P\left\{\begin{array}{lcr} =O & & O= \\ -O-H & & H-O-- \\ \text{———} & O & \text{———} \\ \text{———} & O & \text{———} \end{array}\right\}P,$$

or, $H_2 P_2 O_6 = 2 HPO_3$, for any other formula could only be produced if we suppose the pyrophosphoric acid to be split asunder by the very means which generally unites groups of atoms, namely by the separation of water between two hydroxlye groups. Of course this is merely speculation but the existence of more than one sodium metaphosphate seems to warrant the belief that metaphosphoric acid can appear in polymeric process.

†The metaphosphoric acids are supposed to have the formulæ:

$$H P O_3$$
$$2 (H P O_3) = H_2 P_2 O_6$$
$$3 (H P O_3) = H_3 P_3 O_9$$

or, in general, to be $n (H P O_3)$.

such atoms replaced by that metal. When the secondary phosphates are heated, the pyrophosphate very frequently results, thus:

$$Na_2HPO_4 = Na_4P_2O_7 + H_2O,$$

and when the primary ones are similarly treated the metaphosphate is produced:

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

Only primary and secondary salts of very pronounced metals, such as sodium, potassium and calcium, are known, in other cases the tertiary salt alone exists; therefore when silver nitrate is added to the secondary phosphate of sodium, the insoluble tertiary phosphate of silver is precipitated:

$$Na_2HPO_4 + 3\,AgNO_3 = Ag_3PO_4 + 2\,NaNO_3 + HNO_3,$$

This reaction is one which puzzled the older chemists not a little, for by mixing a solution of two salts which were neutral they obtained a liquid of acid reaction, (because of the nitric acid formed). All secondary and tertiary phosphates, excepting those of the alkali metals and of ammonium, are insoluble in water, while on the other hand all *primary* phosphates are soluble. The tertiary and secondary phosphates therefore are dissolved by acids, the primary phosphates being formed, thus:

$$Ca_3(PO_4)_2 + 4\,HCl = Ca(H_2PO_4)_2 + 2\,CaCl_2\text{[*]}$$

$$\left\{\begin{array}{l}\text{Insoluble tertiary}\\ \text{calcium phosphate}\end{array}\right\} + \text{acid} = \left\{\begin{array}{l}\text{soluble primary}\\ \text{calcium phosphate}\end{array}\right\} + \text{salt.}$$

By the addition of soluble bases to the soluble primary phosphates the insoluble tertiary ones are precipitated;

$$3\,Ca(H_2PO_4)_2 + 12\,NH_4OH = Ca_3(PO_4)_2 + 4\,(NH_4)_3PO_4 + 12H_2O\text{[†]}$$

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[*] See pages 149 and 154.

[†] A reaction such as this is really not as formidable as at first glance it would appear to be. It consists in simply neutralizating the excess of acid hydrogen atoms in the primary salt by means of ammonia. As the tertiary phosphate of calcium is always formed, we must necessarily, in endeavoring to picture by atomic symbols the changes which really take place, use *three* times the formula weight of calcium primary phosphate, because then are *three* atoms of calcium in $Ca_3(PO_4)_2$. The remainder of the work simply consists in counting up how much ammonium hydroxide it will take to replace all of the remaining hydrogen atoms by the group NH_4. A study of this reaction in the laboratory reveals that exactly the proportion by weight of $Ca_3(PO_4)_2$ and $(NH_4)_3PO_4$ expressed in this equation are in reality produced by nature.

The soluble secondary phosphates of the alkali metals are the usual salts of those elements, the insoluble secondary phosphates of pronounced metals like calcium, barium or strontium, which form such salts, are readily produced from these by precipitation:

$$\underset{\text{Soluble.}}{Na_2HPO_4} + \underset{\text{Soluble.}}{CaCl_2} = \underset{\text{Insoluble.}}{CaHPO_4} + \underset{\text{Soluble.}}{2\,NaCl},$$

The soluble *tertiary* phosphates of the alkali metals have a strongly alkaline reaction* and show the greatest tendency to separate a portion of the metal contained in them as the hydroxide.

$$Na_3PO_4 + H_2O = Na_2HPO_4 + NaOH.$$

This characteristic bears out the theory which we developed when discussing phosphorous acid, (pages 215, 216). Phosphoric acid, being a stronger acid than phosphorous acid will have a greater tendency to form sodium salts, so that, while the tertiary sodium *phosphate*, although unstable, really does exist, the tertiary *phosphite* is not known.

All meta phosphates, provided they are not those of a volatile metal-like substance such as ammonium, are unchanged even by quite a high heat, it follows that these salts will be formed under conditions which render the existence of the salts of the great majority of other acids impossible; as a consequence phosphoric acid will ultimately decompose the salts of much stronger acids like sulphuric, leaving a phosphate in their place, while on the other hand in solution or in the cold the exact reverse takes place, i. e., the other acids decompose the phosphates.

Pyrophosphoric acid is quadribasic but only forms two classes of salts, those with $M_4P_2O_7$ and those with $M_2H_2P_2O_7$ as their general formula. On being heated with water the pyrophosphates change into the secondary orthophosphates.

Phosphoric acid is necessary for animal and vegetable life, tertiary calcium phosphate forms the major portion of the inorganic constituents of the bones and teeth, but phosphoric acid combined in some form is also found in the blood, in the muscle and nerve tissues and in the brain. The phosphates which are found in the soil are generally of an insoluble variety, however, the chemical action of the various substances which are present, aided by water, renders them finally partially soluble and absorbable by plants. The primary calcium phosphate has, when mixed with other ingredients, an extensive sale as superphosphate; it is used as a fertilizer.

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*(i. e. they turn red litmus of a blue color (page 71.)

Two other oxides of phosphorus, $P_2 O_4$ and $P_4 O$ are known; they are of little importance except that $P_2 O_4$ is analogous to $N_2 O_4$. A larger work must be consulted for their description.

The following table shows the connection between the compounds discussed in the last two chapters.

$$\left\{\begin{array}{l}\text{The compounds } \underbrace{P\,Cl_3 \quad P_2\,O_3}_{} \ldots\ldots\text{and}\ldots\ldots \underbrace{P\,Cl_5, \quad PO\,Cl_3}_{} \\ \text{with water yield } \quad P\,(OH)_3 \qquad\qquad\qquad\qquad PO\,(OH)_3 \ldots\ldots\ldots \text{less } H_2\,O \\ \qquad\qquad \text{Phosphorous}\ldots\ldots\text{and}\ldots\ldots\text{Phosphoric acid.}\end{array}\right.$$

$P_2\,O_5$
Plus

$H\,PO_3$
Metaphosphoric acid.
$+ H_2\,O$
$H_3\,PO_4$
Orthophosphoric acid.
$+ H\,PO_3$

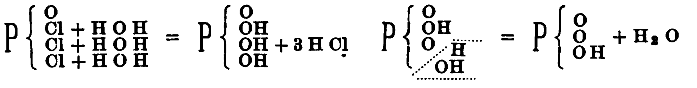
$2\,H_3\,PO_4 - H_2\,O = \ldots\ldots\ldots\ldots H_4\,P_2\,O_7$

Phosphorous acid, $H_3\,PO_3$ can only form primary and secondary salts, $H_2\,M\,PO_3$ and $H\,M_2\,PO_3$.

Metaphosphoric acid, $H\,PO_3$ is monobasic.

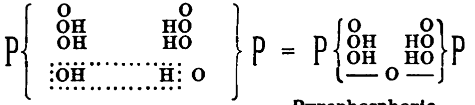
Orthophosphoric acid is tribasic and forms primary, secondary and tertiary salts, $M\,H_2\,PO_4$, $M_2\,H\,PO_4$, $M_3\,PO_4$.

Pyrophosphoric acid, $H_4\,P_2\,O_7$ is quadribasic and forms secondary and quaternary salts, $M_2\,H_2\,P_2\,O_7$ and $M_4\,P_2\,O_7$.



$$P\left\{\begin{array}{l}O\\ Cl + H\,O\,H\\ Cl + H\,O\,H\\ Cl + H\,O\,H\end{array}\right. = P\left\{\begin{array}{l}O\\ OH\\ OH\\ OH\end{array}\right. + 3\,H\,Cl \qquad P\left\{\begin{array}{l}O\\ OH\\ O\;H\\ OH\end{array}\right. = P\left\{\begin{array}{l}O\\ O\\ OH\end{array}\right. + H_2\,O$$

Phosphorus oxychloride. Orthophosphoric acid. Metaphosphoric acid.



$$P\left\{\begin{array}{ll}O & O\\ OH & HO\\ OH & HO\\ OH & H\end{array}\right. O \left.\vphantom{\begin{array}{l}O\\O\\O\\O\end{array}}\right\} P = P\left\{\begin{array}{ll}O & O\\ OH & HO\\ OH & HO\\ - & O -\end{array}\right\} P$$

Pyrophosphoric acid.

Salts of pyrophosphorous acid, analogous to those of pyrophosphoric acid have also been described.

CHAPTER XXXI.

ARSENIC AND ARSINE.

Arsenic, symbol As, atomic weight 75, specific gravity 5.76. Specific gravity of vapor at red heat, air $= 1$ *is 10.3,* $H = 2$ *is 296.6, molecular weight of* $As_4 = 300$, *of* $As_2 = 150$. *Arsine,* $As\ H_3$, *specific gravity, air* $= 1$, *is 2.69,* $H = 2$ *is 77.5, molecular weight 78.021, 1 c. c. of the gas at 0° and .76 m pressure weighs .003495 grams.*

Arsenic occurs quite frequently in the form of the uncombined element, especially in formations which contain the metallic sulphide; the native arsenic is found in greyish black, reniform masses. Combined arsenic occurs in the arsenides of many metals, the chief examples of which are:

Arsenopyrite, Fe As S (corresponding to $Fe\ S_2$ iron pyrites, one atom of sulphur being replaced by one of arsenic.)

Smaltite, (Co, Fe Ni) As_2 (corresponding to $Fe\ S_2$, iron pyrites, both atoms of sulphur being replaced by arsenic.)

Cobaltglance, Co As S.

Two sulphides of arsenic are also found as quite frequent minerals, they are:

$As_2\ S_2$, realgar.
$As_2\ S_3$, orpiment.

In addition to these occurrences, arsenic also appears as the oxide $As_2\ O_3$, and in some arsenates, these latter probably the results of the oxidation of the arsenides. The arsenic of commerce is either the naturally occuring element or it is prepared from the arsenides which are found as minerals.

The two sulphides mentioned above and the oxide $As_2\ O_3$, have been known since ancient times; Aristotle mentions the former, but the term arsenicon seems first to have been used by Dioscorides. The element arsenic does not seem to have been isolated until the latter part of the seventeenth century; of course its chemical nature was not understood until much later.

The commercial preparation of arsenic depends upon the formation of ferrous sulphide and free arsenic, when arsenopyrite is heated:

$$Fe\,As\,S = Fe\,S + As.$$

The impure arsenic so prepared is purified by sublimation, for when heated it volatilizes without previously melting, and then collects on the colder parts of the retorts in crystals.

Arsenic has a steel-grey color and metallic lustre, when fractured it resembles white pig iron. Arsenic, like sulphur and phosphorus, exists in two allotropic forms, one of which is crystalline* and the other amorphous. When the element is heated in a glass tube, amorphous arsenic is deposited on the walls as a black mirror, while the bright, shiny crystals of the other variety appear upon the cooler portions. The amorphous form is changed into the crystalline by heating to 360.° Crystallized arsenic has a specific gravity of 5.76, amorphous of 4.71.

When heated in the air, arsenic burns to form the trioxide $As_2\,O_3$; in this particular the element differs from phosphorus, which, under similar circumstances, forms the pentoxide $P_2\,O_5$. When heated or burned, arsenic has a peculiar odor, somewhat resembling that of phosphine. The element unites directly with chlorine, bromine or iodine to form the corresponding halogene compounds, and arsenic also readily combines with a number of metals, thus yielding arsenides.

Arsenic volatilizes at 450°; the vapors have a lemon yellow color and a most disagreeable garlic odor. Their specific gravity, air = 1, at a low read heat, is 10.3, which, $H = 2$, gives 296.6; the molecular weight at this temperature is therefore 300 and the molecule consists of four atoms, As_4. The density of the arsenic vapors, however, gradually diminishes as the heat is increased, until it reaches 6.5 at 1437°.† The molecules, As_4, which correspond to those of phosphorus, P_4, therefore begin to dissociate as a white heat is reached, so that they change into a mixture of As_4 and As_2‡;—the value for the specific gravity would be 5.22, air = 1, were complete dissociation into As_2 to result.

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* Hexagonal system, rhombohedra.

† Latest determinations by Victor Meyer and Mensching.

‡ Possibly they partially dissociate into the individual atoms, there is no means of determining this point.

Arsenic is an element which is on the boundary line between metal and not-metal. Crystallized arsenic is entirely metallic in appearance, although it is neither malleable nor ductile; it conducts heat and electricity quite readily. Chemically, arsenic is almost entirely a not-metal but its approach to the metallic character is evinced by the instability of its hydrogen compounds.

Arsine, $As\,H_3$, is the analogon of phosphine, $P\,H_3$, and of ammonia, NH_3. It is produced, similarly to phosphine, by the action of an acid upon some arsenide, thus:

$$\underset{\text{Zinc arsenide.}}{As_2\,Zn_3} + 6\,H\,Cl = 2\,\underset{\text{Arsine.}}{As\,H_3} + 3\,Zn\,Cl_2$$

Such a reaction is exactly like the ones which were studied when the preparation of hydrogen sulphide and other hydrogen compounds was discussed, thus:

$$Fe\,S + 2\,H\,Cl = Fe\,Cl_2 + H_2\,S.$$
$$Zn_3\,As_2 + 6\,H\,Cl = 3\,Zn\,Cl_2 + 2\,As\,H_3.$$

This method furnishes pure arsine. Another and more important way of preparing arsine is by the action of nascent hydrogen upon an acid solution of a soluble arsenic compound. For instance, a solution of arsenic trioxide in hydrochloric acid when added to zinc which is covered with dilute sulphuric acid and which is therefore generating hydrogen, will develope arsine, the latter, however, naturally is mixed with hydrogen.

$$As_2\,O_3 + 12\,H = 2\,As\,H_3 + 3\,H_2\,O.$$

The most delicate test for arsenic (Marsh's test) is based upon this chemical fact.[63]

Arsine is a colorless gas, with a most disagreeable odor. It is an intense poison, so that it is imperatively necessary to take every precaution when experimenting with the gas, especially when the latter is obtained pure as it is from zinc arsenide.* The specific gravity of arsine is 2.69, air = 1, or 77.5, H = 2, the molecular weight is therefore 78.021 (As = 75, 3 H = 3.021; As H_3 = 78.021) and the formula As H_3. Arsine changes to a liquid at —102° and forms a white crystalline mass at —119°. When ignited in the air the gas burns with a bluish white flame, forming water and arsenic trioxide, the latter compound appearing in the form of a white smoke. If the air supply in which arsine is burning is limited, or if the flame is cooled, for example by holding a porcelain plate in it, the arsenic formed by the decomposition will separate and will form a dark spot on the surface in contact with it. A mixture of arsine and oxygen explodes violently when ignited.

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* Arsine should *never* be generated otherwise than under a hood or in the open air

Arsine is much less stable than phosphine. When it is passed through a heated glass tube it readily decomposes into hydrogen and arsenic, the latter being deposited as a black mirror. Of course arsine is a powerful reducing agent; sulphuric acid is readily decomposed by it, just as that acid is by hydroiodic acid or hydrogen sulphide, but in this case the acid is robbed of all of its oxygen while the sulphide of arsenic is formed;* other acids and even water or alkali can likewise decompose hydrogen arsenide. Arsine reduces silver nitrate in solution; metallic silver is precipitated and arsenic trioxide is formed; this fact is of importance in the detection of arsenic. The basic properties manifested by ammonia and phosphine are absent in arsine; the latter forms no arsonium compounds; it can only be made to act as a base when the hydrogen atoms contained in it are substituted by some more positive, so-called organic radicle, like methyl.†

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*This would appear to be an example of the nascent action of a solid element like arsenic; the element, at the moment of its liberation from arsine, readily combines with the hydrogen sulphide or perhaps with sulphur formed by the reduction of the sulphuric acid.

† See methane, chapter on compounds of carbon and hydrogen.

CHAPTER XXXII.

THE COMPOUNDS OF ARSENIC WITH THE HALOGENES, WITH OXYGEN AND WITH OXYGEN AND HYDROGEN.

The halogene compounds of arsenic are not complicated by the existence of two series, for only the trihalogene derivatives have with certainty been prepared; their chief characteristics are as follows:

AsF_3, arsenic trifluoride, liquid, boils at 63°.
$AsCl_3$, arsenic trichloride, liquid, boils at 130.2°.
$AsBr_3$, arsenic tribromide, solid, melts at 20–25°, boils at 220°.
AsI_3, arsenic tri-iodide, solid, sublimes when heated.

Arsenic shows its resemblance to the metals and at the same time its connection with the not-metals no where better than in the chemical behavior of its chlorine compound. The latter substance can be formed, *as are the chlorides of metals*, by the action of hydrochloric acid on the trioxide of arsenic, so that in this case arsenic trioxide is a base and arsenic a metal.

$$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O.$$

This formation of the chloride of arsenic is not, however, possible unless very little water is present, it takes place, for instance, when dry hydrochloric acid is passed over the oxide of arsenic, or when the latter substance is distilled with a mixture of sulphuric and hydrochloric acid. On the other hand, when an excess of water is added to the trichloride it is entirely decomposed into hydrochloric acid and arsenic trioxide:

$$\text{a.}\quad 2AsCl_3 + 6H_2O = 2As(OH)_3 + 6HCl,$$
$$\text{b.}\quad 2As(OH)_3 = As_2O_3 + 3H_2O.$$

An arsenious acid which corresponds to phosphorous acid does not exist, where its formation is to be expected, not it, but its anhydride, As_2O_3, results. The easy decomposition of the trichloride of arsenic by an excess of water, therefore, is a phenomenon classing arsenic as a not metal, for the chlorides of the pronounced metals are unchanged by the action of water.[*] The addition of a little water only partially decomposes arsenic trichloride:

$$\mathrm{As}\left\{\begin{array}{l}\mathrm{Cl} + \mathrm{HOH}\\ \mathrm{Cl} + \mathrm{HOH}\\ \mathrm{Cl}\end{array}\right. = \mathrm{As}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{Cl}\end{array}\right. + 2\,\mathrm{H\,Cl}.$$

a so-called basic salt, i. e., a salt which is in part hydroxide and in part chloride being produced, (see antimony trichloride). The chloride, bromide or iodide of arsenic can readily be formed by the direct union of the elements. These compounds are all extremely poisonous substances; the fluoride, chloride and bromide fume in the air, absorb moisture and decompose, leaving the trioxide.

Arsenic forms two oxides, $As_2\,O_3$[†] and $As_2\,O_5$, they are the anhydrides respectively of arsenious and of arsenic acid; arsenious acid is, however, known only in its salts, for we have seen that when it is liberated from these it at once breaks down into its anhydride and water. Owing to the few reactions in which arsenic acts like a metal, the oxides are sometimes named arsenious and arsenic oxides in conformity with the nomenclature usually adopted where a metal forms two such compounds (see pages 24 and 25).

Arsenious oxide (arsenic trioxide, $As_2\,O_3$) is the most common preparation of arsenic, having been known to the ancients and having been a familiar substance ever since the time of the Romans, it is popularly known by the name of arsenic or white arsenic; when cases of poisoning by arsenic occur the substance used is generally "white arsenic." As its name implies, it is a white solid, resembling ordinary flour. The commercial product is formed by roasting the arsenical sulphides which occur as mineral deposits, arsenico-pyrite is especially advantageous for this purpose; in roasting the latter, care must be taken to have a sufficient supply of air, otherwise arsenic, which is formed as shown on page 225, sublimes together with the oxide. Quantities of white arsenic are also produced while burning cobalt, nickel, tin and silver ores; the arsenious oxide is collected in cold chambers and is purified by sublimation. The white arsenic of commerce generally contains traces of the corresponding oxide of antimony.

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[*] See page 77.

[†] The specific gravity of this substance taken by Victor Meyer, above 1500° corresponds to a molecule formula $As_4\,O_6$. The smallest molecule of the trioxide of arsenic with which we are acquainted is therefore $As_4\,O_6$.

Sublimed arsenic trioxide appears in two forms, in the first as a dimorphous substance, crystallizing both in the regular and in the monoclinic system, and in the second as an amorphous, glass-like body, which gradually changes into a porcelain-like mass. The oxide volatilizes at 200°.

Arsenious oxide is a poison to all animals and even to plants. Owing to its tastelessness and the readiness with which it can be mixed with foods, it is frequently used as a poison both intentionally and accidentally. It acts in two ways.

a. As a corrosive substance, attacking the organic surfaces with which it comes in contact, it therefore causes local inflammation in the stomach and intestinal tract.

b. It has a destructive effect on the medullæ of the nerves. The more rapidly the poison is absorbed the less the action under *a* and the more the one under *b* is observed; it follows that the latter is more prominent when the arsenic is administered in solution, and of course it is of material influence whether the stomach is full or empty at the time of taking. .005 gram have a marked effect, and if continued can cause death; .06 to .12 gram may cause death in a few days, and .2 to .3 gram in a few hours. Symptoms: Nausea, salivation, burning in the gastric region, vomit yellow or greenish, and possibly streaked with blood, while traces of white arsenic may be visible therein, great thirst, colic and sensitiveness of the abdomen. The symptoms of the action under *b* are:—intense fear, convulsive movements, trembling and cramps in the extremities; fainting spells and delirium:—where large quantities have been rapidly absorbed the patient may be entirely unconscious. On post mortem examination:—fatty degeneration of the liver and heart as well as in many other organs, the effects of the poisoning being much like those resulting from the taking of phosphorus. An antidote is a mixture of freshly precipitated ferric hydroxide and magnesium oxide, the endeavor being to form the insoluble ferric arsenite. Glass-like arsenic trioxide is much more soluble in water than is the crystallized variety, 100 parts of water at ordinary temperatures dissolve four parts of the former and 1.2 so 1.3 parts of the latter.

The chemical action of arsenic trioxide is twofold, for it can appear both as a base and as the anhydride of an acid.

α. It acts like a base, because it can dissolve in a number of acids. One or two of the salts produced, for instance the chloride $As\,Cl_3$ and a sulphate ($As_2\,(SO_4)_3 + SO_3$), have been isolated, these substances are decomposed by water.

β. It acts like the anhydride of an acid, because it dissolves in bases to form arsenites, which correspond in formula to the nitrites:

$$As_2\,O_3 + 2\,K\,OH = 2\,As\,O_2\,K + H_2\,O.$$

The meta-arsenites (like potassium meta-arsenite $As\,O_2\,K$) are the most common salts of this acid, they correspond to the nitrites $NO_2\,M$; a few orthoarsenites, $As\,O_3\,M_3$, are also known. The arsenites of the alkali metals are soluble in water, the others are either soluble with difficulty or entirely insoluble, they are decomposed by hydrochloric acid. The alkaline solutions of arsenic trioxide are most powerful reducing agents; they have the greatest tendency to take up oxygen to form arsenates, but on the other hand, arsenious oxide is quite readily reduced and a method for detecting arsenic is based upon the ease with which their substance gives up oxygen.[64]

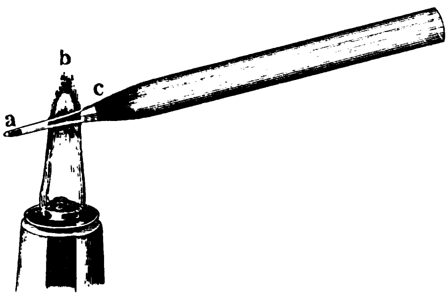

FIGURE 42.

Arsenic pentoxide, $As_2\,O_5$, is the anhydride of arsenic acid, it corresponds to $N_2\,O_5$ and $P_2\,O_5$; three acids, analogous to those of phosphorus, are derived from this oxide; they are:

$H\ As\ O_3$, metaarsenic acid,
$H_3\ As\ O_4$, orthoarsenic acid,
$H_4\ As_2\ O_7$, pyroarsenic acid.

Arsenic pentoxide is produced when arsenic acid is heated to a low red heat, a higher temperature produces decomposition into arsenic trioxide and oxygen. It is a colorless, amorphous mass, which greedily absorbs moisture and finally deliquesces.

Orthoarsenic acid, $H_3 As O_4$, the only arsenic acid which exists in aqueous solutions, is produced by oxidizing arsenic trioxide (for instance by chlorine, bromine or nitric acid.*) When the solution produced by oxidizing arsenic trioxide is evaporated to dryness, orthoarsenic acid separates in needle-like crystals; when these are heated to 180° they separate water and change into pyroarsenic acid:

$$2 H_3 As O_4 = H_4 As_2 O_7 + H_2 O;$$

which latter at 206° changes into meta-arsenic acid.

$$H_4 As_2 O_7 = 2 H As O_3 + H_2 O,$$

and this substance finally at red heat decomposes to yield the anhydride $As_2 O_5$. Each one of these compounds is converted into orthoarsenic acid by solution in water.

Orthoarsenic acid is tribasic and forms primary, secondary and tertiary salts the formulæ of which are, of course, exactly like those of the same derivatives of phosphoric acid, (see page 219). Primary and secondary arsenates, when they are glowed, undergo the same changes which take place with primary and secondary phosphates:

$$\begin{array}{cccccc} MH_2 As O_4 & = & M As O_3 & + & H_2 O. \\ \text{Primary arsenate.} & & \text{Metaarsenate.} & & \\ M_2 H As O_4 & = & M_4 As_2 O_7 & + & H_2 O. \\ \text{Secondary arsenate.} & & \text{Pyroarsenate.} & & \end{array}$$

The arsenates of the alkalis are soluble in water, while only the primary arsenates of the other metals dissolve; it will be remembered that this is also the case with the phosphates.

Arsenic acid is a tolerably good oxidizer, quite a number of reducing agents reduce it to arsenic trioxide. It has of late years been extensively used in the manufacture of aniline dyes because, while it certainly gives up its oxygen, it does not do so with such facility as to destroy the organic substance it acts upon. Sulphur dioxide reduces arsenic acid as follows:

$$H_3 As O_4 + H_2 O + SO_2 = H_3 As O_3 + H_2 SO_4,$$

---

* The pupil should write these equations, using the knowledge acquired in studying the previous oxidizing action of these substances.

the arsenious acid so formed, of course, breaking down into arsenic trioxide and water. This reaction serves to distinguish arsenic acid from phosphoric acid, for the latter substance, although in every respect like the former, has no tendency whatever to give up oxygen and change to phosphorous acid. Arsenic acid is a powerful poison.

CHAPTER XXXIII.

THE COMPOUNDS OF ARSENIC WITH SULPHUR AND WITH SULPHUR AND HYDROGEN.

Arsenic forms three sulphides, two of which correspond in formula to the two oxides; they are $As_2\,S_3$ and $As_2\,S_5$, while the third is the ruby red mineral, realgar, $As_2\,S_2$.

Arsenic trisulphide and arsenic pentasulphide are especially interesting because they act much like anhydrides of oxy-acids and therefore illustrate the marked chemical resemblance between sulphur and oxygen.

Arsenic trisulphide is found as a natural, yellow colored mineral which bears the name of orpiment. It is produced, like the sulphides of many metals, by the action of hydrogen sulphide upon an acidified solution of arsenic trioxide, for the sulphide of arsenic is one of those which are insoluble in dilute acids. (See page 95.)

$$2\ As\,Cl_3 + 3\ H_2\,S = A_2\,S_3 + 6\ H\,Cl.$$

When precipitated it is a bright yellow powder. Arsenic trisulphide can also be formed by direct union of the elements, just as is the trioxide. Arsenic trioxide dissolves in alkaline solutions to form a meta-arsenite:

$$As_2\,O_3 + 2\ K\,OH = 2\ As\,O_2\,K + H_2\,O,$$

and the trisulphide is dissolved by sulphhydrates in exactly the same way:

$$As_2\,S_3 + 2\ K\,SH = 2\ As\,S_2\,K + H_2\,S,$$

in this case potassium metasulpharsenite is formed. Metasulpharsenious acid may be considered as derived from an orthosulpharsenious acid by the separation of hydrogen sulphide, just as meta-arsenious acid could be formed from an orthoarsenious acid; the following equations will make this clear:

$$\mathrm{As}\left\{\begin{matrix}\mathrm{SH}\\ \mathrm{SH}\\ \mathrm{SH}\end{matrix}\right. = \mathrm{As}\left\{\begin{matrix}\mathrm{S}\\ \mathrm{SH}\end{matrix}\right. + \mathrm{H_2\,S}.$$

Orthosulpharsenious acid = Metasulpharsenious acid + Hydrogen sulphide;

$$\mathrm{As}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right. = \mathrm{As}\left\{\begin{matrix}\mathrm{O}\\ \mathrm{OH}\end{matrix}\right. + \mathrm{H_2\,O}.$$

Orthoarsenious acid = Metaarsenious acid + Water.

We saw, however, that metaarsenious acid is incapable of existence, for, when liberated from its salts, it at once breaks down as follows:

$$2\ \mathrm{As\,O_2\,H} = \mathrm{As_2\,O_3} + \mathrm{H_2\,O};$$

metasulpharsenious acid acts in exactly the same way:

$$2\ \mathrm{As\,S_2\,H} = \mathrm{As_2\,S_3} + \mathrm{H_2\,S};$$

and therefore, when acids are added to solutions of the sulpharsenites, arsenic trisulphide is precipitated:

$$2\ \mathrm{As\,S_2\,K} + 2\ \mathrm{H\,Cl} = \mathrm{As_2\,S_3} + \mathrm{H_2\,S} + 2\ \mathrm{K\,Cl}.$$

Arsenic trisulphide can readily be dissolved in the hydroxides of the alkalis, for then a mixture of the arsenite and sulpharsenite is produced;* it is also dissolved by ammonium sulphydrate, only in the latter event a salt of pyrosulpharsenious acid is the result:

$$\mathrm{As}\left\{\begin{matrix}\mathrm{SH} & \mathrm{HS}\\ \mathrm{SH} & \mathrm{HS}\\ \mathrm{SH} & \mathrm{HS}\end{matrix}\right\}\mathrm{As} = \mathrm{As}\left\{\begin{matrix}\mathrm{SH} & \mathrm{HS}\\ \mathrm{SH} & \mathrm{HS}\\ \multicolumn{2}{c}{\mathrm{—S—}}\end{matrix}\right\}\mathrm{As} + \mathrm{H_2\,S}.$$

$$2\ \mathrm{As\,(SH_3)} = \mathrm{As_2\,S_5\,H_4} + \mathrm{H_2\,S}.\quad \text{(See page 223.)}$$

The ammonium pyrosulpharsenite so formed would be

$$\mathrm{As_2\,S_5\,(NH_4)_4}.\dagger$$

Some salts derived from orthosulpharsenious acid, $\mathrm{As\,(SH)_3}$, are also known; none of the acids exists in the free state, they at once break down into the trisulphide of arsenic and hydrogen sulphide when liberated from their salts.

Arsenic pentasulphide can be produced from the trisulphide by fusing the latter with sulphur:

$$\mathrm{As_2\,S_3} + 2\ \mathrm{S} = \mathrm{As_2\,S_5};$$

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* $2\ \mathrm{As_2\,S_3} + 4\ \mathrm{K\,OH} = 3\ \mathrm{As\,S_2\,K} + \mathrm{As\,O_2\,K} + 2\ \mathrm{H_2\,O}$.

† $\mathrm{As_2\,S_3} + 4\ \mathrm{NH_4\,SH} = \mathrm{As_2\,S_5\,(NH_4)_4} + 2\ \mathrm{H_2\,S}$.

this sulphurization corresponding to the oxidation of arsenic trioxide:

$$As_2 O_3 + 2 O = As_2 O_5.$$

Arsenic pentasulphide cannot, like the trisulphide, be precipitated from solutions of arsenic acid by means of hydrogen sulphide, because the arsenic acid is first reduced to arsenious acid by means of sulphuretted hydrogen, which latter substance is oxidized to sulphur, as a consequence a mixture of arsenic trisulphide and sulphur is produced.*

Arsenic pentasulphide dissolves in the sulphides, sulphhydrates or hydroxides of the alkalis to form sulpharsenates—it acts as the anhydride of sulpharsenic acid:

$$A_2 S_5 + 2 K SH = 2 As S_3 K + H_2 S.$$

The sulpharsenates are derived from three sulpharsenic acids, orthosulpharsenic acid, $As S_4 H_3$, corresponding to orthoarsenic acid, $As O_4 H_3$, metasulpharsenic acid, $As S_3 H$, corresponding to metaarsenic acid, $As O_3 H$; and pyrosulpharsenic acid, $As_2 S_7 H_4$, corresponding to pyroarsenic acid, $As_2 O_7 H_4$. When an acid is added to a solution of a sulpharsenate, orthosulpharsenic acid is precipitated:

$$As S_4 K_3 + 3 H Cl = As S_4 H_3 + 3 K Cl.$$

This orthosulpharsenic acid, when boiled, changes to the pentasulphide of arsenic and hydrogen sulphide, just as the orthoarsenic acid changes to arsenic pentoxide and water at a red heat.

$$2 As S_4 H_3 = As_2 S_5 + 3 H_2 S$$
$$2 As O_4 H_3 = As_2 O_5 + 3 H_2 O.$$

When arsenic trisulphide is dissolved in the sulphides of the alkalis containing an excess of dissolved sulphur,† the *sulpharsenates* are found in the solution; the superfluous sulphur sulphurizes the trisulphide just as oxygen oxidizes the trioxide; the pentasulphide so formed of course produces the sulpharsenate by union with the metallic sulphide:

$$As_2 S_5 + K_2 S = 2 As S_3 K.$$

The following table shows the most important facts discussed in this chapter:

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* $H_3 As O_4 + H_2 S = H_3 As O_3 + H_2 O + S$. Zimmermann states that if the solution of arsenic acid is boiling the pentasulphide is precipitated.

† See foot-note page 151.

OXIDES.

$As_2 O_3$, forms no acids, forms meta-arsenites, $M As O_2$, and orthoarsenites, $M_3 As O_3$.

$$As_2 O_5 \begin{cases} As O_3 H, \text{ meta-arsenic acid, forms meta-arsenates.} \\ As O_4 H_3, \text{ ortho-arsenic acid. forms ortho-arsenates.} \\ As_2 O_7 H_4, \text{ pyro-arsenic acid, forms pyro-arsenates.} \end{cases}$$

HALOGENE COMPOUNDS.

Arsenic forms tri-halogene compounds, $As X_3$, but no penta-halogene compounds, $As X_5$.
The tri-halogene compounds are decomposed by an excess of water, forming arsenic trioxide and halhydric acids: $2 As X_3 + 3 H_2 O = As_2 O_3 + 6 H X$.

SULPHIDES.

$As_2 S_3$, forms no acids, forms meta-sulpharsenites, $M As S_2$, ortho-sulpharsenites, $M_3 As S_3$, and pyro-sulpharsenites, $M_4 As_2 S_5$.

$$As_2 S_5, \text{ forms ortho-sulpharsenic acid, } As S_4 H_3, \text{ which yields: } \begin{cases} M As S_3, \text{ meta-sulpharsenates.} \\ M_3 As S_4, \text{ ortho-sulpharsenates.} \\ M_4 As_2 S_7, \text{ pyro-sulpharsenates.} \end{cases}$$

	Arsenites and Sulpharsenites.	Arsenates and Sulpharsenates.
Meta-salts.	$M As O_2$, $M As S_2$.	$M As O_3$, $M As S_3$.
Ortho-salts.	$M_3 As O_3$, $M_3 As S_3$.	$M_3 As O_4$, $M_3 As S_4$.
Pyro-salts.	————, $M_4 As_2 S_5$.	$M_4 As_2 O_7$, $M_4 As_2 S_7$.

CHAPTER XXXIV.

ANTIMONY AND STIBINE. THE COMPOUNDS OF ANTIMONY WITH THE HALOGENES.

Antimony, symbol Sb, atomic weight 120. Stibine, formula $Sb\,H$: specific gravity not determined.

But little antimony is found as the naturally occurring uncombined element; it is most frequently encountered combined with sulphur in the mineral stibnite, $Sb_2\,S_3$, a lead gray substance with metallic lustre, from which most of the antimony of commerce is obtained. Stibnite has been known since the most ancient times. It is mentioned by Dioscorides as *στιμμι* and by Pliny as *stibium*. It was mainly used in medicine for external application, but it also formed a pigment for blackening the eyebrows. The name antimonium was applied to it at a later date. The element and its compounds interested the immediate successors of the alchemists greatly for they thought them to be most wonderful and potent medicinal remedies.

Antimony is prepared from its sulphide by one of two common metallurgical processes; the compound is either melted with iron, by which means ferrous sulphide and antimony are produced, or it is roasted in a draught of air, the sulphur burned off, and the resulting oxide of antimony ($Sb_2\,O_4$) further heated with charcoal, whereupon antimony and carbon monoxide are formed.

Antimony is much more metallic in its nature than is arsenic: its appearance indicates this, for it is silver white, with a metallic lustre; the metal is neither malleable nor ductile, has a crystalline structure,* is brittle and easily pounded into a fine powder: it melts at 425° and is vaporized at a high red heat.† The specific gravity of the vapor of antimony at 1437° is 12.4. This number is, probably by mere accident, the one which should be found were the molecule of antimony Sb_3, so that antimony certainly has no stable molecules of the formula Sb_4 corresponding to those of arsenic and phosphorus, As_4 and P_4. Probably, were it possible to ascertain the specific gravity of antimony at about 1800°, we would find a value which would indicate molecules formed of Sb_2, or perhaps even of the individual atoms.

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* An amorphous form of antimony has also been described.

† This vaporization is much retarded if the element is covered with a layer of oxide.

Antimony, when heated to a high red heat in air or in oxygen, burns to form the trioxide, $Sb_2\,O_3$; it unites with the halogenes in the same way, powdered antimony even glows vigorously when dropped into a flask containing chlorine, while the trichloride, $Sb\,Cl_3$, is produced. Antimony shows its metallic nature, chemically, by dissolving in hydrochloric or sulphuric acid; with the former, it produces the trichloride and hydrogen, with the latter the sulphate of antimony and sulphur dioxide, for as dilute sulphuric acid does not attack the element, reduction of the hot and concentrated acid takes place exactly as it does when that substance is heated in contact with copper. (See pages 72 and 133).

Nitric acid oxidizes antimony, as it did phosphorus or arsenic, but the reaction varies according to the temperature, concentration and mass of the acid, where the latter is cold and dilute, antimony trioxide is formed; as the temperature is increased, or the acid becomes more concentrated, antimonic acid begins to be produced until, under proper conditions, this may be the entire result of the oxidation, of course the nitric acid is reduced at the same time. (See page 198).

Antimony is an ingredient of a number of commercially very important alloys. A combination produced by fusing two or more metals together is called an alloy. Some metals can be alloyed with each other in all proportions, others only partially, while some will not mix at all; an exactly parallel case is found in the behavior of ordinary liquids, some of which, like alcohol and water, can be mixed in any ratio, others, like water and ether, will only partially dissolve each other, while lastly, some oils and water remain entirely separate. The question as to whether alloys are mere mechanical mixtures of fused metals, or whether they have the character of chemical compounds has been the subject of continued discussion and, indeed, the same may be said of solutions, which latter certainly have not the characterists of mere mechanical mixtures. The facts sustaining the theory of chemical combination are as follows. An alloy has a specific gravity different from the mean of the specific gravities of the component metals and a melting point which also is not the mean of the melting points of constituents. The fusing point of a metal is generally diminished by being alloyed, and some alloys melt at a temperature much below that at which any of the constituents fuse. Heat is given off in the formation of alloys [*] while many have a definite crystalline form. Nevertheless those alloys which are produced by metals which mix in any proportion do not have that characteristic which is supposed to be the *sine qua non* of a chemical compound—the definite composition by weight—nor can they be separated into their constituent parts by simple mechanical means. The former discrepancy is explained by the theory that certain definite compounds of the metals are really formed, but that these are further dissolved in the excess of one or the other of the constituents. This theory is borne out by the fact that many such alloys on being slowly cooled, allow mixtures of a definite crystalline form and gravimetric composition to separate in the same way as ordinary solid, chemical compounds can be crystallized from solutions.[†] Those metals which are chemically most like each other generally mix most easily to form alloys. Most metals are white or grey and most alloys are also white or grey; copper and gold are red and yellow respectively, their alloys present modifications of these colors unless the admixture of the added metal is so great in quantity as to entirely conceal this characteristic. Amalgams, as we have already seen, are alloys containing mercury. They are easily fused if, indeed, they are not soft at ordinary temperatures, the mercury evaporates when the amalgam is heated to the boiling point of that element.[‡] Some amalgams have a definite crystalline form and chemical composition. If, as seems unavoidable, we regard alloys as chemical compounds, we must nevertheless believe that they certainly cannot be classed with substances ordinarily considered as such, on the other hand their existence is a constant argument against a too dogmatic conception of the laws of definite proportions and of valence.

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[*] Fused zinc and fused copper when mixed with each other liberate so much heat that the mass may spatter out of the containing crucible.

[†] Rudberg, Poggendorff's Annalen 18, page 31.

[‡] In that way amalgams resemble crystals with water of crystallization.

The most important alloy of antimony is composed of one part of that metal to four of lead, this substance is used as type metal, copper and bismuth are occasionally added to this; the metal used for stereotyping also contains tin.

The hydrogen compound of antimony is called stibine. It is produced, like arsine, by the action of acids on the alloy of antimony and zinc * or by the action of nascent hydrogen on soluble compounds of antimony, the gas is therefore produced by the same means which furnish arsine, as a consequence the latter may contain stibine unless care is taken to exclude that gas; in fact stibine may be mistaken for arsine unless especial precautions are taken to distinguish between the two.[65]

Stibine is a colorless and odorless gas, scarcely soluble in water. As would be expected, owing to the metal-like nature of antimony, this gas is much less stable than arsine, it can be compared to hydrogen telluride (page 99) in this respect, for it partially decomposes into antimony and hydrogen, even at —56°. From this instability it follows that stibine cannot be obtained free from hydrogen at ordinary temperatures. Stibine changes to a liquid at —91.5° and solidifies at —102.5°, forming a snow like mass; when passed through a heated glass tube it decomposes into antimony and hydrogen, just as arsine does into arsenic and the latter element; the antimony is deposited in the form of a mirror which is more metallic in appearance than is the one formed of arsenic and which furthermore is not readily votalized. When lighted, stibine burns with a white flame, giving off a dense smoke of the trioxide of antimony; a spot of metallic antimony will form on a cold porcelain plate held in the flame. Of course chlorine, bromine or iodine attack stibine, producing the corresponding halogene compound of antimony.

As the basic properties of the hydrogen compounds of the elements of this family have disappeared when arsine is reached, it follows that stibine can form no salts corresponding to those of ammonium and phosphonium.

Another, solid, compound of antimony and hydrogen has been described, to this the formula Sb_4H has been ascribed, its existence, however, is doubtful.

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* The alloy consists of three parts zinc to two of antimony.

Antimony forms two series of compounds with the halogenes, $Sb X_3$ and $Sb X_5$, they correspond to those of phosphorus.

$Sb F_3$, solid.
$Sb Cl_3$, solid; soft crystalline mass, melts 73°, boils 233°, specific gravity air = 1 is 8
$Sb Br_3$, solid; melts 90°. boils 265.°
$Sb I_3$, solid; boils 420.°
$Sb F_5$, not crystalline, gum-like mass.
$Sb Cl_5$, fluid; melts —6, can be distilled without decomposition in a vacuum.
$Sb I_5$, solid; melts 78° and decomposes when heated to a higher temperature.

The trihalogene compounds can be produced by direct union of the elements, and the pentahalogene compounds by addition of halogenes to the trihalogene compounds. The trichloride has been most thoroughly studied and its chemical behavior will serve as an example for that of the other haloid compounds. The trichloride is, as would be expected, much less readily decomposed by water than the corresponding trichloride of arsenic, indeed, it can even be dissolved in tolerably dilute hydrochloric acid without decomposing. When it is added to water it does not completely break down, but changes into a so-called basic salt.

A basic salt is one which is formed by the interaction of less of the acid and more of the base than is necessary to form the normal salt.

We can consider all oxides of the metals which act as bases as being derived from the corresponding hydroxides by loss of water, the manner of formation being similar to that of the anhydrides:

$$H_2 SO_4 - H_2 O = SO_3; \quad Ca (OH)_2 - H_2 O = Ca O,$$
$$2 P (OH)_3 - 3 H_2 O = P_2 O_3; \quad 2 Fe (OH)_3 - 3 H_2 O = Fe_2 O_3.$$

With this in mind we can define a basic salt as one in which only a portion of the hydroxyle groups of a base have reacted with an acid to form a salt and water; it is therefore the reverse of a so-called acid salt, (page 137 and foot note) in which only a portion of the hydrogen in an acid has been replaced by a metal. The same nomenclature can therefore be adopted with both classes of salts and the terms primary, secondary and tertiary basic salts can be used. When water is added to the trichloride of antimony the following reaction takes place:

$$Sb \left\{ \begin{matrix} Cl + HOH \\ Cl + HOH \\ Cl \end{matrix} \right. = Sb \left\{ \begin{matrix} OH \\ OH \\ Cl \end{matrix} \right. + 2 H Cl.$$

The compound $Sb\,(OH)_2\,Cl$ is therefore the primary basic chloride of antimony; the two hydroxyle groups contained therein can afterward separate water, as follows:

$$Sb\left\{\begin{matrix}OH\\OH\\Cl\end{matrix}\right. = Sb\left\{\begin{matrix}O\\Cl\end{matrix}\right. + H_2\,O.$$

The compound $Sb\,O\,Cl$ is therefore also a basic salt. In this case the group of elements $Sb\,O$ is a radical which chemically resembles a monovalent metal, as a comparison of the following formulæ will make clear:

$(Sb\,O)\,Cl$,*
$Na\,Cl$,
$K\,Cl$.

The monovalent radicle $Sb\,O$ is sometimes called stibionyl and is quite frequently encountered in the basic salts of antimony, such an instance is found in the formula of the sulphate: $(Sb\,O)_2\,SO_4$.

Those metals which have not a very pronounced metallic character are the ones which form basic salts, metals like sodium, potassium or calcium do not so so.

Antimony trichloride can combine with the chlorides of a number of metals to form double chlorides with formulæ like the following, $Sb\,Cl_3\,3\,K\,Cl$, more extended mention of these will be made in the chapter on aluminum.

The pentachloride of antimony is an unexpectedly stable compound; it can be boiled in a vacuum without change and, furthermore, it is not decomposed by cold water but forms a crystalline substance containing the latter compound as water of crystallization.

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*More complicated basic chlorides than this one also exist, for their study the student must refer to a larger work.

CHAPTER XXXV.

THE COMPOUNDS OF ANTIMONY WITH OXYGEN AND WITH OXYGEN AND HYDROGEN. THE SULPHIDES OF ANTIMONY.

Antimony forms the following oxides, $Sb_2 O_3$, $Sb_2 O_4$, $Sb_2 O_5$, only the last one of these is a pronounced acidic anhydride, indeed, the trioxide acts as a base when brought in contact with pronounced acids.

Antimony trioxide is found in nature as the mineral senarmontite. It can be formed by burning antimony or by oxidizing the element with dilute, boiling nitric acid. Chemically it acts just like the corresponding oxide of arsenic, it dissolves in alkaline hydroxides to form meta-antimonites:

$$Sb_2 O_3 + 2 KOH = 2 Sb O_2 Na + H_2 O.$$

Two hydroxides derived from this oxide are known, one, which might be called pyro-antimonous acid, has the formula, $Sb O_5 H_4$, the other is the normal hydroxide, $Sb (OH)_3$; corresponding to orthophosphorous acid, $P (OH)_3$. Antimony trioxide dissolves in pronounced acids to form salts in which antimony is the metal, so, for instance, it produces the trichloride with hydrochloric acid:

$$Sb_2 O_3 + 6 H Cl = 2 Sb Cl_3 + 3 H_2 O.$$

The salts formed with other than the halhydric acids are basic ones, insoluble in water while the trichloride, formed by the above reaction, is also converted into the insoluble basic cloride by adding water to the acid solution (see page 242). Antimony trioxide is easily reduced to the metal by heating with charcoal or in hydrogen. When heated in the air it takes up oxygen and changes to the tetroxide, $Sb_2 O_4$, which substance is likewise formed from the pentoxide by heating, so that $Sb_2 O_4$ is the most stable of the oxides of antimony. The trioxide is but little soluble in water.

The pentoxide of antimony, $Sb_2 O_5$ is produced by oxidizing antimony with fuming nitric acid, (page 193) or with aqua regia (page 193); it loses oxygen at red heat and changes into the tretroxide, $Sb_2 O_4$.

The basic properties of $Sb_2 O_3$ have been entirely destroyed by adding the two oxygen atoms necessary to form $Sb_2 O_5$,—so that the latter substance forms no salts with acids.

The following acids derived from antimony pentoxide are known, they correspond to those of phosphorus and of arsenic, and are:

$Sb O_3 H$,	meta-antimonic acid,
$Sb O_4 H_3$,	ortho-antimonic acid,
$Sb_2 O_7 H_4$,	pyro-antimonic acid,

and $Sb_2 O_9 H_8$, a hydrated pyro-antimonic acid formed as follows:

$$Sb_2 O_7 H_4 + 2 H_2 O = Sb_2 O_9 H_8.$$

The acid $H_8 Sb_2 O_9$ changes into ortho-antimonic acid on standing with water; it is converted into pyro-antimonic acid at 100°; pyro-antimonic acid forms meta-antimonic acid at 200° and this is finally converted into the anhydride $Sb_2 O_5$ at 300°.

Only two sulphides of antimony, $Sb_2 S_3$ and $Sb_2 S_5$ are known with certainty. They are entirely analogous to the corresponding arsenic compounds.

The trisulphide, $Sb_2 S_3$, has already been mentioned as the mineral antimonite. On roasting in a current of air it is changed, first into the trioxide, $Sb_2 O_3$, and then into the tetroxide $Sb_2 O_4$. The amorphous sulphide is produced by the addition hydrogen sulphide to an acidified solution of antimony trioxide, just as the corresponding arsenic compound is formed. It is dark, orange colored powder, insoluble in water or dilute acids,* soluble in alkaline hydroxides or sulphides, by disolving in the latter it forms an ortho-sulphantimonite, in this way antimony differs from arsenic, which produces the metasulpharsenite under similar circumstances.

$$Sb_2 S_3 + 6 KSH = 2 Sb S_3 K_3 + 3 H_2 S.†$$

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* Under certain conditions antimony trisulphide can be obtained in a from which is soluble in water. Schulze, Journal für Praktische Chemie, [2] 27, 320.

† Compare with the following

$$Sb_2 O_3 + 6 KOH = Sb O_3 K_3 + 3 H_2 O.$$

(The reaction for the formation of antimonite and sulphantimonite by dissolving $Sb_2 S_3$ in alkaline hydroxides is given under arsenic, page 235, foot note). When the alkaline sulphide contains dissolved sulphur, the sulphantimonate is produced, just as is the case with arsenic.

Antimony pentasulphide can be formed by adding sulphuretted hydrogen to a solution containing antimonic acid;* it bears a complete resemblance to the corresponding arsenic compound, dissolving in alkaline sulphides or hydroxides to form sulphantimonates, the majority of which are salts of the ortho acid H_3SbS_4. Only the salts of the alkalis and alkaline earths† are soluble in water. The pentasulphide of antimony is precipitated and hydrogen sulphide is formed when acids are added to solutions containing the sulphantimonates.

It is scarcely necessary to add a table of the antimony compounds, as they correspond so completely to those of arsenic, one fact can be reiterated, namely that antimony can form pentahalogene derivatives while arsenic is unable to do so.

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* Difference between antimony and arsenic.

† The alkaline earths are calcium, barium and strontium.

CHAPTER XXXVI.

BISMUTH. THE COMPOUNDS OF BISMUTH WITH THE HALOGENES, WITH OXYGEN, WITH OXYGEN AND HYDROGEN AND WITH SULPHUR.

Bismuth. Simbol Bi. Atomic weight 208.9.

Bismuth, the element having the highest atomic weight in this family is, as would be expected, entirely a metal, although its compounds correspond in formula to those of the other members.

The metal is found, generally uncombined, in company with cobalt, nickel, silver and lead ores, in gneiss and other crystalline rocks and in clay slate. The most frequent compound is the oxide Bi_2O_3 which occurs in earthy masses called bismite; the sulphide, bismuthinite, Bi_2S_3 and the telluride, tetradymite, $Bi_2(TeS)_3$ are also met with.

It has not been ascertained with certainty how early in the history of metallurgy bismuth became known; it was formerly confused with a number of minerals, all of which went by the name of marcasite. It first became known as a new metal in the fifteenth century, and was called *bisemat* or *wisemutum*, but was even then confounded with antimony; at the end of the eighteenth century, however, it was universally considered to be a metal.

Bismuth, like antimony, is prepared from its ores by roasting the sulphide with iron or the oxide with charcoal. The metal which finds its way into commerce contains small quantities of arsenic and iron; the natural metal is nearly chemically pure. The bismuth, which is to be used in the preparation of compounds intended for pharmaceutical purposes, is subjected to special processes of purification, for all arsenic must be removed from it.

Bismuth is a reddish metal with a pronounced metallic lustre and a coarse crystalline structure. Its specific gravity is 9.8. The metal is brittle, neither malleable nor ductile and can readily be pounded into a powder. It melts at 270° and, in solidifying, expands just as water does in forming ice. It boils at about 1400°; the specific gravity of its vapor at white heat, (1600°—1700°) is 10.1. The calculated specific gravity, were the molecule Bi_2, is 14.4, and is 7.2 if the same were composed simply of individual atoms; as the number 10.1 is less than that which would be found were the molecule diatomic, as in Bi_2, it follows that the vapor of bismuth consists, in part at least, of the individual atoms. At a slightly higher temperature than that of the experiment the molecular and atomic weights of bismuth would probably be identical.

Dilute hydrochloric or sulphuric acids do not attack bismuth, concentrated hydrochloric acid has but little effect; hot and concentrated sulphuric acid dissolves it, forming the sulphate of bismuth and sulphur dioxide, (see page 133); nitric acid quite readily forms the nitrate, while it is itself reduced. (See page 198.)

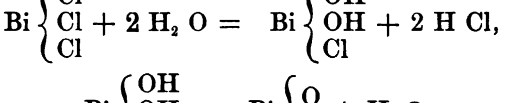
A number of alloys of bismuth are commercially important; they all have low melting points, for example a mixture of five parts of bismuth, three of lead, two of tin and three of cadmium fuses at 65°. One of the chief uses of these alloys is in the copying of wood cuts and in stereotyping.

The halogenes form the following compounds with bismuth:

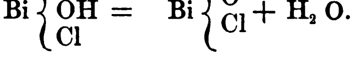
$Bi\,F_3$ bismuth trifluoride,
$Bi\,Cl_3$ bismuth trichloride,
$Bi\,Br_3$ bismuth tribromide,
$Bi\,I_3$ bismuth tri-iodide.

All of these compounds are solid bodies at ordinary temperatures. The existence of other halogene derivatives is doubtful.

The trihalogene compounds can either be formed by the direct union of bismuth with chlorine, bromine or iodine, or by dissolving the trioxide, $Bi_2\,O_3$, in concentrated halhydric acids, this oxide of bismuth being entirely basic in its character. The chloride or bromide of bismuth can be dissolved in very little water or in acids; they, however, decompose on the addition of an excess of water just as do the corresponding antimony compounds, (see page 242) while at the same time the insoluble basic chloride or bromide is formed:



$$Bi\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right. + 2\,H_2\,O = Bi\left\{\begin{matrix}OH\\OH\\Cl\end{matrix}\right. + 2\,H\,Cl,$$



$$Bi\left\{\begin{matrix}OH\\OH\\Cl\end{matrix}\right. = Bi\left\{\begin{matrix}O\\Cl\end{matrix}\right. + H_2\,O.$$

The iodide of bismuth is decomposed only by boiling water, it is insoluble in cold water. The halogene compounds of bismuth form a number of double salts which will be discussed later; these double salts are of the formula

$$Bi\,Cl_3,\ 2\ K\,Cl \text{ and } Bi\,Cl_3,\ K\,Cl.$$

The following oxides of bismuth are known:

$Bi\,O$, bismuth monoxide, brownish black, crystalline powder,
$Bi_2\,O_3$, bismuth trioxide, light yellow powder,
$Bi_2\,O_4$, bismuth tetroxide, dark brown powder,
$Bi_2\,O^5$, bismuth pentoxide, brown powder.

None of these oxides are the anhydrides of acids. The one with least oxygen, $Bi\,O$, is produced by the reduction of salts derived from the oxide $Bi_2\,O_3$;* it is insoluble in water and, when dry, oxidizes in the air so readily that while producing the trioxide the compound burns like a piece of tinder.

Bismuth burns at a high red heat, forming the trioxide, $Bi_2\,O_3$. This substance can more readily be prepared by the addition of potassium hydroxide to a solution of a bismuth salt. The first product formed is the hydroxide, $Bi\,(OH)_3$, which is insoluble in water.

$$Bi\,(NO_3)_3 + 3\ KOH = Bi\,(OH)_3 + 3\ KNO_3.$$

This reaction is a usual one with most metals, for by far the greater number of metallic hydroxides are insoluble in water. The following reactions are typical:

$$Fe\,SO_4 + 2\ KOH = K_2\,SO_4 + Fe\,(OH)_2,$$
$$Cu\,SO_4 + 2\ KOH = K_2\,SO_4 + Cu\,(OH)_2,$$
$$Mg\,(NO_3)_2 + 2\ KOH = K_2\,SO_4 + Mg\,(OH)_2.$$

In each of these cases the insoluble hydroxide is precipitated by the addition of a soluble hydroxide to the salts of the metals. The hydroxides of the alkalies are the only ones which are perfectly soluble in water, those of the metals calcium, barium and strontium are partially so, all others are insoluble. Those hydroxides of the metals which are not dissolved by water are generally converted into the corresponding oxides by the application of a very moderate heat. The hydroxide of bismuth loses water below 100°, and is converted into a compound having the formula $Bi\,O_2\,H$.*

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* By treating solution of chloride of bismuth, in hydrochloric acid, with stannons chloride, $Su\,Cl_2$.

$$Bi\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right. = Bi\left\{\begin{matrix}O\\OH\end{matrix}\right. + H_2\,O,$$

and this, lastly, at boiling heat, is changed to the trioxide.

$$2\,Bi\,O_2\,H = Bi_2\,O_3 + H_2\,O,$$

just as nitrous acid changes into water and $N_2\,O_3$.

The various salts of bismuth are produced by dissolving the oxide or the hydroxides in acids. The chloride has already been discussed, the only other ones we need mention are the nitrate and sulphate.

Bismuth Nitrate.— $Bi\,(NO_3)_3 + 5\,H_2\,O$. Prepared by dissolving either the element bismuth or the oxide, or one of the hydroxides in nitric acid. $Bi_2\,O_3 + 6\,HNO_3 = 2\,Bi\,(NO_3)_3 + 3\,H_2\,O$. Clear, large crystals which melt at 80° in their water of crystallization and which then give off nitric acid, forming the basic nitrate at 120°.

Basic Bismuth Nitrate.—(Subnitrate of bismuth) $Bi\,ONO_3 + H_2\,O$† or

$$Bi\left\{\begin{matrix}OH\\OH\\NO_3.\end{matrix}\right.$$

Formed by decomposing the nitrate with hot water. Insoluble in water. It is a primary basic salt in which one hydroxyle group has been replaced by the group NO_3, on heating in a platinum dish it changes to the oxide $Bi_2\,O_3$, giving off nitric acid. The salt $Bi\,ONO_3$ can be considered as derived from the hydroxide $Bi\,O_2\,H$, by replacing the hydroxyle group with NO_3.

$$Bi\begin{matrix}O\,H\\O\end{matrix} + HNO_3 = Bi\begin{matrix}O\\NO_3\end{matrix} + H_2\,O.$$

The subnitrate of bismuth is the most important salt of bismuth, being extensively used in medicine.

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* This hydroxide is the one corresponding to nitrous acid $N\,O_2\,H$.

† More complicated formulae have been assigned, for these a larger manual must be consulted.

BISMUTH SULPHATE.— $Bi_2 (SO_4)_3 + 7 H_2 O$. Prepared by dissolving the oxide in concentrated sulphuric acid and then adding water. At 100° it changes to $Bi_2 (SO_4)_3 + 3 H_2 O$. Boiling water changes it into the insoluble basic sulphate.

$$S\left\{\begin{array}{l} O\ Bi\ O \\ O\ Bi\ O \\ O \\ O \end{array}\right. = (Bi\ O)_2\ SO_4,$$

The univalent group Bi O corresponds to stibionyl, (page 243).

The pentoxide of bismuth, $Bi_2 O_5$, is produced by oxidizing the trioxide by means of hydrogen peroxide. It is an orange or brown colored powder which forms but one hydroxide, the latter corresponding to the meta acids. This hydroxide, $Bi O_3 H$, is changed to the oxide $Bi_2 O_5$ on heating. Neither the oxide or hydroxide have basic or acid properties.

$Bi_2 O_4$ has been considered as a compound formed by replacing the hydrogen of $Bi O_3 H$ by the univalent group of elements Bi O acting as a metal.

$$Bi\ O\ Bi\ O_3 = Bi_2\ O_4.$$

The sulphides of bismuth correspond to the oxides Bi O and $Bi_2 O_3$. Bismuth monosulphide, Bi S is of little importance. Bismuth trisulphide is found in nature as the mineral bismuthinite. It can be produced by fusing bismuth and sulphur together, or it can be formed by the action of hydrogen sulphide on a solution of a bismuth salt:

$$2\ Bi\ Cl_3 + 3\ H_2\ S = Bi_2\ S_3 + 6\ H\ Cl.$$

The sulphide of bismuth, like the oxide, has no resemblance in its action to the acidic anhydrides, it cannot be dissolved in the hydroxides or sulphides of the alkalies to form sulpho-salts. On the other hand it is readily attacked by concentrated hydrochloric acid to form the trichloride of bismuth and hydrogen sulphide:

$$Bi_2\ S_3 + 6\ H\ Cl = Bi\ Cl_3 + 3\ H_2\ S.$$

Nitric acid dissolves it to form the nitrate of bismuth, while the hydrogen sulphide which is formed is, of course, oxidized by the excess of nitric acid to form sulphur and finally sulphuric acid.

The elements of the nitrogen family, as we have seen, show the same graduation in properties with increasing atomic weights as was displayed by the elements belonging to the sulphur group. This is best brought to light by the following table:

ATOMIC WEIGHTS.	USUAL PHYSICAL CONDITION.	MELTING POINTS.	BOILING POINTS.	SPECIFIC GRAVITY.	NOT METALLIC.
N 14.03	a gas.	—203°	—193	— —	
P 31.	yellow solid, easily fused.*	44°	250°	1.82	
As 75.	steel grey, brittle crystalline,	about 520° †	800° †	5.76	
Sb 120	silver white. brittle, crystalline.	about 425°	about 1100°	6.77	
Bi 208.9	redish mettalic, brittle, crystalline.	270°	about 1600°.	9.8.	metallic.

SPECIFIC GRAVITY OF VAPORS.

N, air = 1, .9713, H = 2, 27.9, molecule N_2.
P, " 4.16, H " 119.8, molecule P_4, at white heat, air = 1, 3. molecule P_2.
As. " 10.3, H " 296.6, molecule As_4; at 1437°, air = 1, 6.7, molecules As_4 and As_2.
Sb, " 12.4, H " 357.1, molecule probably Sb_3.
Bi. " 10.1, H " 290, molecules probably partly Bi_1 and Bi_2.

HYDROGEN COMPOUNDS XH_3, X_2H_4, X_3H.

		HEAT OF FORMATION.	STABILITY			BASIC PROPERTIES.	
N	NH_3	120 K		N_2H_4	N_3H	$NH_3 + HI = NH_4I$	The stability and basic properties diminish with increasing metallic properties of elements, only ammonia and phosphine combine with acids to from salts.‡
P	PH_3	43 K		P_2H_4	P_4H_2	$PH_3 + HI = PH_4I$	
As	AsH_3	-441 K		——	As_2H_2	AsH_3	
Sb	SbH_3	——		——	——	SbH_3	
Bi	—	——		——	——	——	

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*Red phosphorus is changed to yellow at 261°, it then melts. Specific gravity, 2.08 to 2.14.

†Arsenic volatilizes without previously melting, unless it is under pressure.

‡Phosphine forms only a limited number of phosphonium salts, these are decomposed by water. The compound N_2H_4 forms salts with acids, P_2H_4 does not. N_3H is acid in its character, resembling H Cl, H Br and H I.

CHLORINE OOMPOUNDS, XCl_3, XCl_5.

N	NCl_3	liquid, explosive,	——		*Completely decomposed by water as follows: $XCl_3 + 3H_2O = X(OH)_3 + 3HCl$. †Partially decomposed by water, forming basic chlorides as follows: $XCl_3 + 2H_2O = X(OH)_2Cl$; $X(OH)_2Cl = XOCl + H_2O$. The pentachlorides with water yield phosphoric or antimonic acid.
P	PCl_3	" decomposed by H_2O*	PCl_5	Solid	
As	$AsCl_3$	" " " " *	——	——	
Sb	$SbCl_3$	solid " " " †	$SbCl_5$	Solid.	
Bi	$BiCl_3$	" " " " †	——		

OXIDES, HYDROXIDES, SULPHIDES AND SULPHO SALTS.

Oxides.
X_2O, X_2O_3, X_2O_5,

OXIDES.					SULPHIDES.			
N_2O	——	——	——		——		——	——
NO	——	——	——	BiO	——	As_2S_2	——	——
N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3	P_2S_3	As_2S_3	Sb_2S_3	Bi_2S_3
N_2O_4	P_2O_4	——	Sb_2O_4	Bi_2O_4	——	——	——	——
N_2O_5	P_2O_5	As_2O_5	Sb_2O_5	Bi_2O_5	P_2S_5	As_2S_5	Sb_2S_5	——

The acids derived from the oxides X_2O_3 are formed according to the types $X(OH)_3$, orthoacids; XO_2H, metaacids; $H_4X_2O_5$, pyroacids. Nitrogen only forms the meta-acids and salts derived from this, phosphorus forms only the ortho-acids, but salts of the two other ones are known, arsenic froms no hydroxides, the salts of the meta-arsenious acid are the most frequent, antimony forms the hydroxides corresponding to the ortho and pyroacid, the meta antimonites are the most frequent, bismuth forms the hydroxide $Bi(OH)_3$, it has no acid properties. The tri oxides of nitrogen and phosphorus are acidic only, those of arsenic and antimony are both basic and acidic, that of bismuoh is basic only.

The pentoxides are all acidic with the exception of that of bismuth, which is neither acidic or basic, the acids derived from the oxides X_2O_5 are formed according to the types XO_4H_3, orthoacids; XO_3H, meta acids; $X_2H_4O_7$ pyroacids. Nitrogen only forms the meta acid, NO_3H, bismuth forms one hydroxide BO_3H, not acid in its nature.

The sulphides As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5 are insoluble in water; they dissolve in alkaline sulphides to form salts of sulphoacids. These acids are exactly like the oxygen acids with the exception that, in them, sulphur has taken the place of oxygen, atom for atom. The sulphides P_2S_3, P_2S_5 are decomposed by water. the sulphide Bi_2S_3 has no acidic properties.

CHAPTER XXXVII.

THE ELEMENTS OF THE CARBON FAMILY.

The elements of the carbon family are carbon, silicon, germanium, tin and lead. The same changes as were observed in the preceeding family are caused by the increase in the atomic weights belonging to the elements in this one, but, as the whole family is less not-metallic than that of which nitrogen is the representative, only two of the elements, namely carbon and silicon, can form hydrogen compounds; the transition from not-metal to metal takes place after the second member of the group.

The alterations in the physical properties of the isolated elements shows this increasing metallic character for, while carbon and silicon are found either in the form of amorphous, black elements or crystalline bodies which, in the case of diamond, may even be transparent, germanium, tin and lead have a brilliant metallic lustre. Germanium and tin, however, have a crystalline structure, while lead is the only member of the family which is perfectly malleable and ductile. The fusing points of the elements under discussion diminish with increasing atomic weights, while the specific gravities increase.

Carbon; infusible, possibly softens in the heat of the electric arc; specific gravity (as graphite) 2.1.

Silicon; fuses in the heat of the electric arc; specific gravity (graphitoidal) 2.49.

Germanium; melts at about 900°; specific gravity 5.46.

Tin; melts at 238°; specific gravity 7.29.

Lead; melts at 325°; specific gravity 11.44.

The general formula for the hydrogen compounds of the elements of the chlorine family is $X H$; for those of the hydrogen compounds of the oxygen and nitrogen families the formulæ are respectively $X H_2$ and $X H_3$, in the carbon family the corresponding compounds are $X H_4$. With the number of four hydrogen atoms to one of the other element, the power of fixing hydrogen which is possessed by not-metals is exhausted, indeed, no elements other than those we have considered, are capable of forming definite gaseous hydrogen compounds. It follows that the maximum valence which any element displays toward hydrogen is four, (see pages 102, 103). The relationship between the groups of elements and the formulæ of the hydrogen compounds becomes more apparent if we arrange those which we have studied in the order of their atomic weights, reversing the order observed in the table on page 171:

ELEMENTS.				HYDROGEN COMPOUNDS.				RELATION TO ATOMIC WEIGHTS.
C	N	O	F	CH_4	NH_3	OH_2	FH	As we pass from left to right the atomic weights of the elements on any horizontal line increase, while the valence toward hydrogen diminishes. No elements with atomic weights lying between those of any two on any horizontal line are known. These elements are therefore a section of that table which would be obtained by arranging all of the elements in the order of their increasing atomic weights.
12	14	16	19	SiH_4	PH_3	SH_2	ClH	
Si	P	S	Cl		AsH_3	SeH_2	BrH	
28	31	32	35.5		SbH_3	TeH_2	IH	
—	As	Se	Br					
	75	79	80					
—	Sb	Te	I					
	120	125	127					

The elements given on the above table are the only ones which are capable of forming gaseous hydrogen compound. Of course the stability of the hydrogen compound of silicon is less than that of carbon, for the rule is without exception that with increasing atomic weight, in any given family, there is a diminution in the stability of the hydrogen compounds.

Carbon possesses in the most eminent degree that property which we observed in a rudimentary form in the hydrogen compounds of nitrogen, namely, the element can form an almost unlimited number of complicated hydrogen compounds, derived from a nucleus of carbon atoms united one with the other, just as the two nitrogen atoms are in hydrazine (page 185). As many as thirty-five carbon atoms are known to be thus united in a long and simple chain, while the variety of compounds may be almost indefinitely increased by branching side chains or by the formation of rings of atoms each of which can serve as a nucleus for further substitution or addition. The study of these compounds forms, at present, a separate branch of chemistry, which is generally termed organic chemistry, although, of course, there is no real distinction between this and so-called inorganic chemistry. A few of the simpler carbon and hydrogen compounds will be taken up in the course of this work.

All of the elements of the carbon family form dioxides, $X O_2$, and all but silicon exhibit a monoxide, $X O$. The dioxides of carbon, silicon, germanium and tin have the character of acidic anhydrides, that of tin, however, like the trioxide of arsenic, can be both acidic and basic, for it dissolves both in acids and bases to form salts. The monoxide of carbon is neither acidic nor basic, that of germanium is slightly basic, the other monoxides are all basic in their character and form well-defined salts with acids.

The acids derived from the dioxides have the general formulæ $H_2 X O_3$ and $H_4 X O_4$, the former being the meta-acids, the latter the ortho-acids; they are all unstable, readily losing water and leaving the corresponding anhydride $X O_2$, indeed, it is doubtful if carbonic acid exists at all, even in aqueous solution. The silicic acids, both ortho and meta, are changed to silicon dioxide when heated; they lose a large amount of water even when dried at ordinary temperatures, so that the existence of hydrated silicic acids of definite formula is doubtful. Germanium dioxide apparently forms no hydrates; the stannic acids, both ortho and meta, are completely dehydrated when glowed. Lead dioxide has no acidic properties.

All of the carbonates are derived from a meta-carbonic acid, $H_2 CO_3$, only a few organic derivatives of ortho-carbonic acid, $H_4 CO_4$ are known. Both ortho and meta silicates exist and form two classes of frequently occurring minerals, while salts of much more complicated silicic acids which are formed by the separation of water between two or more formula weights of the ordinary acids are quite common. Both ortho and meta-stannic acid, $H_4 Sn O_4$ and $H_2 Sn O_3$, are known, although all salts are derived from the latter compound. The relationship is made more apparent in the following table:

Oxides.	Meta-acids.	Ortho-acids.	Meta-salts.	Ortho-salts.
CO_2	H_2CO_3*	——†	M_2CO_3	——†
SiO_2	H_2SiO_3*	H_4SiO_4*	M_2SiO_3	M_4SiO_4,
GeO_2	——	——	M_2GeO_3‡	——
SnO_2	H_2SnO_3	H_4SnO_4	M_2SnO_3	M_4SnO_4
PbO_2	——	——	——	——

* Existence as acids doubtful.

† Only orthocarbonates of organic compounds are known.

‡ More thorough investigation of germanium salts is necessary.

The monoxides, with the exception of that of carbon, are bases, they dissolve in acids to form a number of well-defined salts which, when compared with those of the lower oxide of the elements of the preceeding family, show a similar, though not quite so well marked tendency to change into basic salts on the addition of water.

The following sulphides, corresponding to the oxides, have been studied:

——	Carbon disulphide, CS_2.
——	Silicon disulphide, SiS_2.
Germanium monosulphide, GeS;	Germanium disulphide, GeS_2
Stannic monosulphide, SnS;	Stannic disulphide, SnS_2.
Plumbic monosulphide, PbS;	——

The disulphide of silicon is too unstable to enter into other compounds, indeed, it is even decomposed by the moisture of the air, but the other disulphides dissolve in the sulphides of the alkali metals to form sulpho salts which in formula correspond to the oxygen salts.

The chlorine compounds and chlorine and oxygen compounds are formed after the general formulæ XCl_2 and XCl_4 and $XOCl_2$. Of course, a representative of each of these classes is not known for every element in the family; the most important ones will be individually discussed in the succeeding chapters.

CHAPTER XXXVIII.

CARBON.

Carbon; Symbol C, atomic weight, 12.

The element carbon occurs in three modifications, two of which, diamond and graphite, are of crystalline structure, while the third is amorphous carbon and occurs widely distributed in the form of coal. By far the greater quantity of carbon, however, is found combined in the numerous compounds of that element. Carbon dioxide, as was mentioned on page 62, is an essential constituent of the atmosphere. The carbonate of calcium forms limestone, chalk, marble and the two crystalline minerals, calcite and arragonite; the carbonates of calcium and magnesium, under the name of dolomite, are the principal structure of great masses of rock, and furthermore, the carbonates of iron, zinc, barium, manganese and lead are important additions to the mineral wealth of the world. Carbon is also invariably present in all of the innumerable organic compounds with which we are acquainted, while, furthermore, those products of vegetable disintegration which are classed under the head of coal, are, in the main, composed of the element under discussion,

Carbon is dimorphous; as diamond it crystallizes in the regular system, while as graphite it is monosymmetric.*

The diamond occurs chiefly in the older alluvial deposits, but has been found imbedded in a laminated granular quartz rock called itacolumite; it is also found in a species of conglomerate composed of rounded siliceous pebbles, quartz, and chalcedony. It was originally imported into Europe from the East Indies, from which portion of the world and from Borneo the only specimens were procured until 1727 when large diamond fields were discovered in Brazil. In 1867 the diamond fields of South Africa were opened.

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* Formerly supposed to be hexagonal.

Some diamonds are also found in the Urals, in New South Wales and in the United States.

The diamond is distinguished by its extreme hardness, its brilliancy of reflection and adamantine lustre, its specific gravity is 3.5 and it is a poor conductor of electricity and of heat. The mineral also occurs in black pebbles or masses known as *carbonado*, having a specific gravity of from 3.01 to 3.4. A coarse variety of diamond which, owing to imperfections in structure, is unfit for jewelry is sold for glass cutting purposes, under the name of *bort*. The weight of the diamond is measured in carats (1 carat = .205 gram) the price per carat increases in geometric ratio, although always modified by the quality of the stone. The largest diamond is about the size of half a hen's egg, it originally weighed 900 carats, but was greatly reduced in weight by cutting; the Pitt or Regent diamond weighs 135.25 carats and is of unblemished transparency and lustre. When not in contact with the air, diamond can be heated to a white heat without alteration, when heated between the carbon points of an arc light it swells and changes to a greyish mass with an almost metallic lustre, in this form it resembles ordinary coke. When heated in the air, diamond takes fire at about 1000° and then burns to form carbon dioxide (CO_2) leaving only a very slight trace of ash. Oxidizing agents such as fused potassium nitrate or potassium bichromate and sulphuric acid can oxidize diamond to carbon dioxide. Sir Humphrey Davy was the first to prove that diamond consisted of nearly pure carbon.

Graphite, also called plumbago or black lead, is the second crystalline form of carbon. It occurs in beds and imbedded masses in the oldest geologic formations, in granite, gneiss, micaceous schists and crystalline limestone. It is probably in some instances the result of the alteration by heat of deposits of coal; although its origin is as yet imperfectly understood. In some places the graphite is found quite pure, for instance in the "Eureka Black Lead Mine" at Sonora, California, there is a bed from twenty to thirty feet in thickness which contains the substance in so pure a state that it can be cut in blocks and shipped without further preparation. The ash left on burning this graphite is only about five per cent. of the whole. Sometimes the graphite is, of course, much more impure, so that it may be entirely unfit for use. The chief occurrences of the mineral are in the Urals in Siberia; in Borrowdale, Cumberland; in Arendal, Norway, and in some parts of Austria, Russia and France, while large quantities are found in the East Indies. In the United States the mineral occurs quite frequently, notably in California; at Sturbridge, Mass.; at Ticonderoga and in the northern part of Michigan. Graphite can be artificially prepared by crystallization of carbon which has been dissolved in melted iron, for when grey pig iron is dissolved in acids the insoluble graphite remains in the form of small delicate scales, a similar form of the substance has also been discovered in some meteorites.

Graphite is used in the manufacture of lead pencils and infusible crucibles and as a lubricator, the substance being soft and scaly. It is greyish black and has almost a metallic lustre. When burned in the air it forms carbon dioxide, leaving an ash, which, when derived from the purer varieties, consists mainly of ferric oxide and silica. When heated with nitric acid for some length of time, graphite changes to a yellow, crystalline body which contains carbon, hydrogen and oxygen, resembles organic substances and is known as graphitic acid. The latter substance, when heated, disintegrates with an almost explosive violence, leaving a voluminous black residuum which apparently consists of very finely divided graphite. This latter form of the substance is applied as a covering to the moulds used in electroplating, for, as graphite is a good conductor of electricity, it renders the surfaces of the non-conducting substances from which these are made, capable of conducting electricity, an essential preliminary to the formation of a metallic deposit.

Those compounds which are formed in animal and vegetable organisms, and which are classed under the general head of organic substances, are produced by the union of a very few elements, namely carbon, hydrogen, oxygen, nitrogen, sulphur and phosphorus. When such substances decompose in the open air they break down completely, changing for the most part into gaseous products, but when the vegetable fibres are protected by a layer of water, as is the case in peat-bogs the process of decomposition goes on slowly, certain portions of the constitnents of the organic substances, especially oxygen and hydrogen, generally pass off in other combinations while the vegetable substance becomes changed, first into peat and then into bituminous coal and at the same time the percentage of contained carbon increases. Peat, brown coal, bituminous coal and anthracite coal are successive steps in the process of floral decomposition; when the anthracitic stage is reached the changes become so complete that a black, shiny, homogeneous mass has resulted in which the original vegetable structure has entirely disappeared or is at least so indistinct that special means must be taken for its detection. The pressure to which the dead organic structures are subjected is of material influence on the rapidity with which a peat formation is changed to anthracite, indeed, in portions of Russia where the coal has not been subjected to great pressure a brown coal (lignite) which can be scarcely distinguished from peat, is found in places where the age of the deposit would lead one to expect anthracite. A comparison of the approximate composition of the combustible portions of some of the varieties of coal will show the changes more clearly:

Wood,	**Carbon**	**50**	**p'r c't;**	**hydrogen**	**6**	**p'r c't;**	**oxygen**	**and**	**nitrogen**	**44**	**p, c.**
Peat,	"	60	"	"	5.75	"	"	"	"	34.25	"
Lignite,	"	67	"	"	5.3	"	"	"	"	27.7	"
Bituminous coal,	"	87	"	"	5.6	"	"	"	"	7.4	"
Anthracite, "	"	94	"	"	3.4	"	"	"	"	2.6	"

The various forms of coal are amorphous, differing markedly from diamond or graphite, which are crystalline.

When organic substances are heated without access of air they undergo a process of carbonization; the volatile products of this destructive distillation pass off as gases and liquids (see page 177) while amorphous carbon is left behind as coke and the same change takes place when bituminous coal is heated.[66] Coke is a porous, shiny form of amorphous carbon; it conducts electricity and heat about as well as graphite. Coke may contain as much as 91.5 per cent. of its total weight in the form of carbon.

Gas coal, which collects on the walls of retorts in which bituminous coal is heated to form illuminating gas, is a product of the decomposition of gaseous compounds of carbon and hydrogen. It has almost a metallic lustre, resembling very dense coke; it is difficult to ignite and conducts heat and electricity quite well.

Wood charcoal is produced by the imperfect combustion of wood sticks, animal charcoal by a similar treatment of such animal refuse as bones or blood. The finer forms of bone charcoal are known as bone black and ivory black. All forms of charcoal, but especially the varieties of animal charcoal, have a remarkably pronounced tendency to absorb coloring matters from solutions.[67] These colored substances are apparently deposited on the surface of the coal, for they can be extracted therefrom by the proper solvents,* while, furthermore, this property of absorbing coloring matter does not belong to charcoal alone, all insoluble, porous substances can perform the same office in a greater or less degree † and in rare instances it may happen that the charcoal exercises a reducing action on the absorbed matter. Crude sugar is decolorized by means of charcoal.

The purest form of amorphous carbon is lamp black, which results from the combustion of carbon and hydrogen compounds where an imperfect supply of oxygen is provided, or where the flame is cooled before perfect combustion has taken place; lamp black is therefore deposited on a cold porcelain or metal plate placed within a luminous gas or lamp flame. The lamp black of commerce is obtained by burning resinous pine wood, tar, or some kinds of bituminous coal. The substance is collected on coarse cloths hung over the burning wood placed in suitable chambers. Lamp black is used in the manufacture of printers' and india ink.

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* Indigo, which has been dissolved in sulphuric acid and absorbed from this solution by charcoal, can be extracted from the charcoal by alkalis. Metallic oxides, absorbed by charcoal can be extracted by strong acids.

† Aluminium hydroxide, ferric hydroxide or precipitated sulphide of lead can absorb coloring matter.

CHAPTER XXXIX.

THE COMPOUNDS OF CARBON WITH HYDROGEN.

Methane, formula CH_4, *specific gravity, air = 1, is .5531, H = 2, is 15.93, molecular weight 16.028. 1 cc. of the gas at 0° and 760 mm. weighs .0007082 grams.*

The simplest hydrogen compounds of the carbon family have the formula XH_4, where X represents an atom of some element of that family, as a consequence the valence toward hydrogen possessed by the atoms of the elements of this group is greater by one than is valence of those of the preceding (nitrogen) family.

Methane, or marsh gas, the hydrogen compound of carbon which corresponds to ammonia in the nitrogen family, occurs quite frequently in nature as a product of the decay vegetable tissues. The muddy bottom of any stagnant marshy pool, when stirred, emits bubbles of marsh gas, which, however, always contain from ten to twenty per cent. of carbon dioxide, as well as a small amount of nitrogen. The metamorphoses which resulted in the formation of coal beds, having been similar to the changes taking place in marshes, must necessarily also have produced methane, so that, as a consequence, pockets of the gas which is sometimes under great pressure, occur quite frequently in coal mines; the escaping gas, when a pocket is tapped, forms a dangerously explosive mixture with the air. Methane in some places escapes from openings in the ground, the gas which is passing of is not infrequently ignited, either intentionally or accidentally; these burning gas wells are sometimes regarded with superstitious reverence, as, for instance, the holy fire at Baku on the Caspian sea.

The natural gas which is used so extensively for illuminating and heating purposes in a number of places in the United States consists for the most part of methane. Methane is always produced in large quantity by the dry distillation of coal, it therefore forms the major portion of illuminating gas.

Methane cannot be prepared by direct union of the elements carbon and hydrogen, yet if hydrogen can be brought to act upon carbon when the latter is in what may be considered the nascent state, it will then unite with that element. An example of such a production of methane is found in the reaction between carbon monoxide (CO) and hydrogen under the influence of a strong discharge of electricity from an induction coil.

$$CO + 6\,H = CH_4 + H_2O.^*$$

The best method to prepare methane for laboratory use is by the dry distillation of some organic substance, and, as we have seen, our choice of which one to select is not very limited. Experience has shown, however, that a mixture of some dry acetate with a strong base will yield methane; an example of the production of the gas in this way can be found in the decomposition of the acetate of sodium when than substance is heated in the presence of sodium hydroxide.

$$CH_3COO\,Na + Na\,OH = CH_4 + Na_2\,CO_3$$

Sodium acetate — Sodium hydroxide — Methane — Sodium carbonate.

Sodium acetate can be considered as methane in which one hydrogen atom has been replaced by the group $COO\,Na$.

Methane is a colorless gas, without odor or taste. Its specific gravity is 0.559. Under a pressure of one atmosphere methane boils at −164°, if evaporated quickly under diminished pressure the liquid will be cooled to below its freezing point and will form a snow like mass. The gas burns in oxygen or air with a nearly colorless flame which is much like that of hydrogen, while carbon dioxide and water are formed.

$$CH_4 + 4\,O = CO_2 + 2\,H_2O.$$

Methane is decomposed into its constituent elements only at quite a high heat, when passed through a white hot tube it breaks down into carbon and hydrogen, it is therefore, with the exception of

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* A similar and most interesting production of methane is by the action of copper on a mixture of the vapors of carbon bisulphide and hydrogen sulphide.

$$8\,Cu + 2\,H_2S + CS_2 = 4\,Cu_2S + CH_4.$$

Here the carbon and the hydrogen may both be considered to be in the nascent state, the copper simply removes sulphur and leaves the carbon and hydrogen to rearrange themselves into the most stable configuration under existing conditions. (See pages 51 and 77).

ammonia, more stable than any of the hydrogen compounds of the preceding family. Methane, when mixed in a eudiometer tube with exactly enough oxygen to form carbon dioxide, can be exploded by means of an electric spark; if care is taken to keep the water vapor produced by this reaction in the form of a gas, the result is that one volume of methane with two of oxygen forms one volume of carbon dioxide and two of water; the total volume of the mixture of gases is therefore the same after the explosion as it was before.

$$\boxed{CH_4} \qquad \boxed{O_2}\boxed{O_2} \quad = \quad \boxed{CO_2} \qquad \boxed{H_2\,O}\boxed{H\,O_2}$$

1 vol. methane, + two vol. oxygen, 1 vol. carbon dioxide. 2 vol. water.

From these results it follows that one molecule of methane is able to form two molecules of water vapor and consequently, as two molecules of water vapor contain four atoms of hydrogen, methane must also have four hydrogen atoms in its molecule. The specific gravity of methane, H = 2, is 15.9, this shows that its corrected molecular weight must be 16,* for when methane is analyzed we find it composed of 12 parts of carbon and 4 parts of hydrogen which form 16 parts of methane. The 4 parts of hydrogen, as we have seen, represent four atoms; that 12 parts of carbon represent one atom we presume to be the case because in no compound of carbon, *the specific gravity, and hence the molecular weight of which is known*, has carbon ever been found to enter with a less proportional weight than twelve; after considering these experimental facts we conclude that the formula of methane is CH_4. (See page 180.)

When methane is mixed with chlorine and placed in the dark no reaction takes place, but when the mingled gases are exposed to the sunlight a violent explosion results; hydrochloric acid and carbon being produced. This action is exactly parallel to the action of chlorine on all other hydrogen compounds with the exception of hydrofluoric and hydrochloric acids:

$$\begin{aligned} CH_4 + 4\,Cl &= C + 4\,H\,Cl, \\ NH_3 + 3\,Cl &= N + 3\,H\,Cl, \\ SH_2 + 2\,Cl &= S + 2\,H\,Cl, \\ Br\,H + Cl &= Br + H\,Cl. \end{aligned}$$

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* In exact numbers 16.028 because the atomic weight of hydrogen is 1.007, in considerations of this kind it is better to neglect the decimal.

When, however, the chlorine is allowed to attack methane slowly, as it does in diffused light, *substitution* of hydrogen for chlorine results, so that the following changes successively take place:

$$\begin{aligned}
CH_4 + 2\,Cl &= CH_3\,Cl + H\,Cl,\\
CH_4 + 4\,Cl &= CH_2\,Cl_2 + 2\,H\,Cl,\\
CH_4 + 6\,Cl &= CH\,Cl_3 + 3\,H\,Cl,\\
CH_4 + 8\,Cl &= C\,Cl_4 + 4\,H\,Cl.
\end{aligned}$$

When one hydrogen atom has been removed from methane, the unsaturated univalent radicle (see page 113) is called *methyl*, when two hydrogen atoms are removed the bivalent radicle is *methylene*, and when three hydrogen atoms are removed the trivalent radicle is methine:

$CH_3 -$, methyl; $CH_3\,Cl$, methyl chloride.
$CH_2 =$, methylene; $CH_2\,Cl_2$, methylene chloride.
$CH \equiv$, methine; $CH\,Cl_3$, methine chloride (chloroform.)

These chlorinated substances can therefore all be considered as methane in which one, two or three atoms of hydrogen have respectively been replaced by chlorine; they partake more or less of the nature of methane, although the introduction of successive chlorine atoms causes the resulting compound to depart more and more from the character of the type, thus:

Methyl chloride is a gas, colorless, becomes liquid at —23.7°.
Methylene chloride, liquid, boils at 41.6°.
Methine chloride, liquid, boils at 61.2°.
Carbon tetrachloride, liquid, boils at 76.5°.

With the introduction of each chlorine atom the boiling point increases and therefore each of these changes brings the character of the chlorine substituted methane farther from that of the colorless gas from which it is derived.

When hydrogen is removed from methane the resulting unsaturated monovalent group, methyl, cannot exist alone any more than can a free atom of hydrogen, it therefore seeks the first opportunity of uniting with some atom or radicle to form a saturated compound. We have seen that when chlorine is present the methyl reacts with that element to form methyl chloride; if no such other substance with which methyl is capable of union can be found, the radicle will join with itself to form dimethyl or ethane; $CH_3 - CH_3$.* Dimethyl is capable of having from one to six of its hydrogen atoms substituted by chlorine. The first reaction which takes place between ethane and chlorine is as follows:

$$CH_3 - CH_3 + 2\ Cl = CH_3 - CH_2\ Cl + H\ Cl.$$

The compound $CH_3 - CH_2\ Cl$ or $C_2\ H_5\ Cl$ is called ethyl chloride, just as $CH_3\ Cl$ is called methyl chloride. If, however, we remove one hydrogen atom from ethane to form the monovalent, unsaturated radicle ethyl, the latter, if no other substance is present with which it can unite, will form diethyl or butane, just as methyl formed dimethyl or ethane.

$$\underset{\text{Ethane} - \text{hydrogen} = \text{ethyl.}}{CH_3-CH_3-H = CH_3-CH_2};\ \underset{\text{ethyl} + \text{ethyl}}{CH_3-CH_2- + CH_3-CH_2-} = \underset{\text{diethyl or butane.}}{CH_3-CH_2-CH_2-CH_3.}$$

Diethyl can likewise have its hydrogen atoms substituted by chlorine and, by the loss of one atom of hydrogen; can be converted into the monovalent, unsaturated radicle butyl, which further unites with itself to form dibutyl or octane. It is possible, however, to so modify the above reaction as to bring ethyl and methyl together, in which case the two radicles will unite to form ethylmethyl or propane † and in the same way a mixture of propyl and ethyl will yield propylethyl or pentane. By a judicious combination of the iodides of other radicles, carbon and hydrogen compounds containing as many as thirty-five carbon atoms have been prepared. These substances, as they contain only carbon and hydrogen, are called hydrocarbons, the particular class of saturated hydrocarbons now under discussion being called paraffins. The first seven representatives of this class are:

CH_4, methane; $C_4\ H_{10}$, butane.
$C_2\ H_6$, ethane; $C_5\ H_{12}$, pentane,
$C_3\ H_8$, propane; $C_6\ H_{14}$, hexane,
$C_7\ H_{16}$, heptane.

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* Methyl iodide treated with zinc or with sodium forms *ethane*. The reaction takes place as follows:

$$CH_3\ I + Zn + CH_3\ I = Zn\ I_2 + CH_3 + CH_3.\quad CH_3 + CH_3 = CH_3 - CH_3.$$

This reaction is also applicable in the formation of the more complicated compounds which follow. Of course, in these cases, we would not use methyl iodide and zinc, but would employ the iodides of those radicles which we wish to unite.

† By treating a mixture of ethyliodide and methyliodide with zinc, thus:

$$\underset{\text{Ethyliodide} + \text{methyliodide}}{CH_3 - CH_2\ I + Zn + CH_3\ I} = \underset{\text{ethylmethyl or propane.}}{Zn\ I_2 + CH_3 - CH_2 - CH_3}$$

A general formula for these compounds is $C_n H_{2n+2}$, where n represents the number of carbon atoms in the chain, an increase of this number by one in any given paraffin raises the boiling point of that paraffin by about 19°. The compounds which begin the series are gases, those with from five to sixteen carbon atoms are liquids at ordinary temperatures, the remainder are solids with melting points ranging from 18° to 74°, the specific gravity of the hydrocarbons increases with the number of carbon atoms, but is always less than one.

The hydrocarbons $C_n H_{2n+2}$ are found in coal oil; this is generally technically divided as follows:

Petroleum ether,	boiling	point	50° to 70°;	pentane and hexane.
Benzine,	"	"	70° to 90°;	hexane and heptane.
Ligroine,	"	"	90° to 120°;	heptane and octane.
Petroleum, (kerosene)	"	"	150° to 300°;	octane to hexadecane ($C_{16} H_{34}$).

The higher boiling portions are vaseline and paraffin.

If one hydrogen atom is removed from ethane, the resulting unsaturated radicle ethyl cannot exist alone, we saw that it unites with itself to form diethyl or butane. Experience has shown us, however, that an entirely different result may be expected if we simultaneously remove a hydrogen atom from each of the carbon atoms contained in ethane, the molecule containing the pair of neighboring carbon atoms which have thus become unsaturated is capable of independent existence and is called ethylene.

$$CH_3 — CH_3, \text{ ethane, } CH_2 — CH_2, \text{ ethylene.}$$

What is true of ethylene remains true when the hydrogen atoms of that substance are substituted by other atoms or groups of atoms: we can therefore, beginning with ethylene as a nucleus, by replacing the hydrogen atoms with ethyl, methyl propyl, etc., construct a new series of unsaturated carbon compounds which would have the general formula $C_n H_{2n}$. A further discussion of these complicated substances belongs in the domain of organic chemistry. The facts that carbon atoms are never known to be unsaturated in organic compounds unless those unsaturated atoms are side by side* and that carbon is tetravalent in methane have led chemists to regard the carbon atoms in ethylene as being joined to each other in a different way than they are in ethane, for, if we suppose the carbon atoms to be always quadrivalent, then the pair of carbon atoms in ethane is joined by one valence of each atom, where in ethylene it is united by two. The following diagram will make this more clear:

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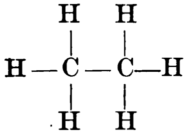
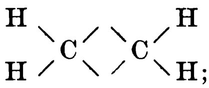
*A few compounds recently discovered may prove to be an exception to this rule.


Ethane.


Ethylene.

the theory being that each valence of any carbon atom must neutralize a corresponding valence of some other atom. All we can know regarding such combinations is that the carbon atoms in any such compound as ethylene are held together by a certain force, of the nature of which we are ignorant, and which we call chemism or chemical affinity. It is usually stated that "carbon has four points of affinity, or four valences;" of course, provided we consider chemism as a force, such a theory is not tenable, because no force can act unless it has something to act upon; when the carbon atoms are united as they are in ethylene a certain amount of residual force beyond that required to hold these two atoms together, acts upon and retains the four hydrogen atoms, this much we know from experimental evidence, but if we further suppose that the carbon atoms are each joined by two points of affinity we must then accept the proposition that the force which unites the two atoms is manifest only from four distinct spots upon their surfaces, an hypothesis which is not in accord with what we know as regards the attraction which one mass exercises toward another; a statement which would more nearly accord with our experimental knowledge would be that in ethylene we have two trivalent, and hence unsaturated, carbon atoms joined to each other.* If by some means we remove a hydrogen atom from each of the neighboring carbon atoms in ethylene, there results a compound CH—CH which is called acetylene. The carbon atoms in acetylene are supposed to be united by a so-called "tripple linking," for the theory which was used in explaining the constitution of ethylene must compel the supposition that the two additional unsaturated valences in acetylene must neutralize each other, the formula of the latter substance is therefore written $CH \equiv CH$; in this case we also must indulge in speculation if we wish to go farther than to assume any more than the existence of two divalènt unsaturated carbon atoms in acetylene.

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* Recent investigations in organic chemistry seem to show that carbon atoms react as if they had the form of regular tetrahedra. The hydrogen atoms in methane would then be at the points of the tetrahedron and the two carbon atoms in ethylene would be joined along the line connecting two of these points. By this hypothesis the difference between saturated and unsaturated carbon chains can be explained.

Ethylene is a colorless gas which is poisonous; it has a specific gravity of .9852, is tolerably soluble in water, and when heated breaks down into methane and carbon:

$$C_2H_4 = CH_4 + C.$$

Owing to this latter decomposition ethylene burns with a luminous flame. Acetylene is a gas which undergoes a similar decomposition:

$$C_2H_2 = CH_4 + 3\,C,$$

and therefore it also emits a luminous flame, for in each case the glowing particles of carbon emit the light.

Illuminating gas, prepared by the distillation of soft coal, is composed chiefly of hydrogen, methane, ethylene and acetylene, carbon monoxide and carbon dioxide. The quality of the flame is determined by the amount of ethylene and acetylene present, for a gas which contains these unsaturated hydrocarbons burns with a luminous flame, while methane or carbon monoxide scarcely give any light during combustion.

A flame can be observed wherever a gas, in consequence of chemical action, is heated sufficiently to cause it to glow. In most cases this chemical reaction is caused by chemical union; that it is possible, however, to have a flame resulting from the heat of decomposition of an endothermic compound is proved by the appearance of a flash accompanying the explosion of nitrogen chloride. The simplest case of flame production can be illustrated by mixing two gases which are capable of giving off a large amount of heat in their union and igniting the mixture by means of an electric spark or by means of a flame. In this mixture the molecules of the two gases are intimately intermingled, the reaction takes place almost simultaneously at all points throughout the volume of the gas and is therefore accompanied by an explosion and the formation of a homogeneous flame.

The most common form of flame is produced by a stream of gas pouring into a volume of another with which it can chemically unite; if the entering gas is heated to its kindling temperature then union will take place along the boundary where the two gases touch. The conical shape assumed by the flame of a gas escaping from a round vent is caused by the diminution in the quantity of that gas as the distance from the opening increases, this diminution being caused by the consumption of the gas in burning. The structure of the flame of a gas burning in air can be taken as a type of all others. Such a flame consists of a number of zones which can be easily distinguished by their appearance. The flame of a candle, for instance, exhibits a dark center which is surrounded by a conical, luminous zone; a piece of paper placed over this, as is shown in Fig. 43, will be charred in the form of a circle, this experiment showing that the gases in the center of the flame are not heated to a high temperature, at the same time a small piece of phosphorus placed in the dark center will not burn, so that no oxygen can be present. Outside of this central cone there is a luminous zone of some thickness where the oxygen is uniting with the escaping gases, but, as oxygen cannot enter into this portion of the flame in excess, the carbon, separated from the glowing gases* by reason of the high temperature of the flame, is not completely burned but is only heated to a white heat. Oxygen is present in excess on the outer surface of the luminous zone and therefore combustion is most energetic in this division of the flame, so that an enveloping mantle which is scarcely visible results; this is the hottest part of the flame. The glowing carbon which causes a flame to become luminus is produced by the breaking down of the heated hydrocarbons present in the gas, a change similar to that undergone by ethylene taking place:

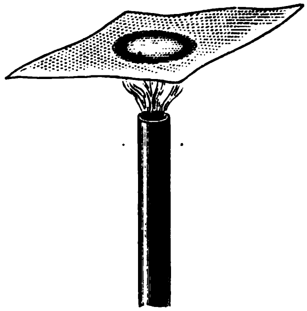

FIGURE 43.

$$C_2H_4 = CH_4 + C.$$

From this it follows that if the temperature of the flame can be lowered to such a point as to prevent this decomposition, the flame will become not luminous; such an alteration can be brought about by diluting the gases before burning;[69] with some indifferent substance, such as carbon dioxide, and the same result can be accomplished by providing a supply of air to the illuminating gas befor the vent at which the flame is lighted is reached. The Bunsen burner attains this end by causing the gas which is escaping from a small central opening to traverse a wider brass tube before ignition. At the bottom of this brass tube two holes are pierced, allowing the entrance of a limited supply of air. This air mingles with the escaping gases, and thus provides for complete combustion before the decomposition of the hydrocarbons takes place. Undoubtedly the non-luminous character of the Bunsen flame is also in part brought about by the addition of the indifferent gas nitrogen, which must necessarily enter the burner in company with oxygen. If the gases composing a flame can be cooled below their kindling temperature, the flame will be extinguished.

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* See ethylene and acetylene.

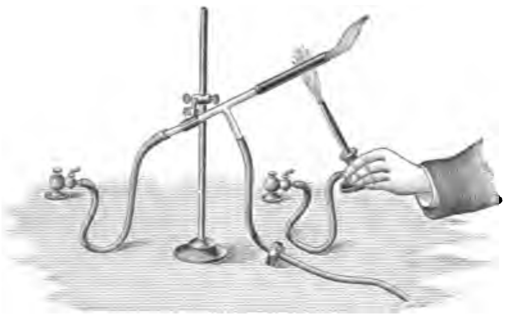


FIGURE 44.

From what has been said regarding the formation of a flame it follows that it is a matter of indifference which of the two gases uniting to form the flame is entering and which forms the surrounding medium, for the phenomena are caused solely by the union of the two. The terms "combustible" and "a supporter of combustion," as applied to gases, are therefore used simply because it is more usual to see gases burning in oxygen or air than it is to see oxygen or air burning in other gases. Of course, the phenomena attendant upon union with oxygen also appear with other gases, which, as chlorine for example, act like oxygen.

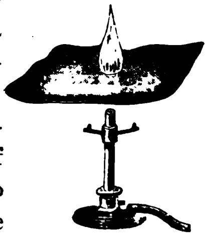


FIGURE 45.

CHAPTER XL.

THE COMPOUNDS OF CARBON WITH CHLORINE, WITH CHLORINE AND OXYGEN, WITH OXYGEN AND WITH SULPHUR.

Carbon dioxide, formula CO_2*; specific gravity, air = 1, is 1.529;* $H = 2$ *is 44, molecular weight 44; one cc. of the gas at 0° and .76 m. weighs .001977 grams. Carbon monoxide, formula* CO*; specific gravity, air = 1, is .96744;* $H = 2$ *is 27.8, molecular weight 28; 1 cc. of the gas at 0° and .76 m. weighs .0012511 grams.*

The only chloride of carbon which need be mentioned in this work is the tetrachloride $C\,Cl_4$; some more complicated chlorine derivatives of carbon chains are known, but a work on organic chemistry must be consulted in regard to their properties. Carbon tetrachloride is derived from methane by replacing all of the hydrogen atoms with chlorine, and it can be prepared, as we have seen, from the latter substance by the action of chlorine; it is not, however, practically expedient to commence with methane in order to produce the tetrachloride, because methine chloride ($C\,H\,Cl_3$, chloroform) is easily procured by other means, and then, beginning with this

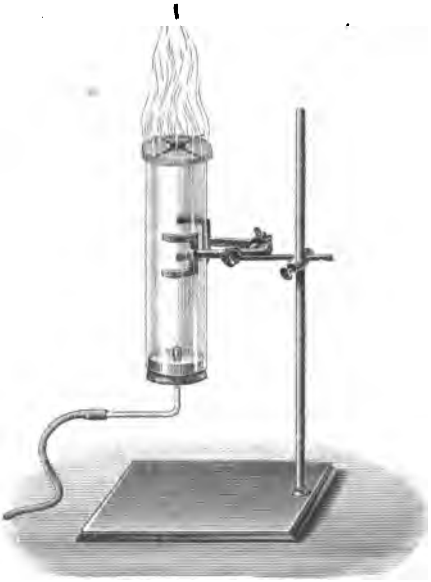


FIGURE 46.

chlorinated methane we can, by passing chlorine into the boiling liquid, finally substitute the remaining hydrogen atom:

$$CH\,Cl_3 + 2\,Cl = C\,Cl_4 + H\,Cl.$$

Carbon tetrachloride is a colorless liquid which boils at 76.5° and which, unlike most of the chlorides of the not-metals, is but slowly decomposed by cold water; on warming with an excess of water it is, however, readily converted into carbonic and hydrochloric acids, but carbonic acid, like all acids whose anhydrides are gases, at once breaks down into its anhydride and water, so that, although we may consider orthocarbonic acid to be the first result of the reaction, carbon dioxide is the only tangible carbon compound produced:

$$1.\quad C\begin{cases} Cl + H\,OH \\ Cl + H\,OH \\ Cl + H\,OH \\ Cl + H\,OH \end{cases} = C\begin{cases} OH \\ OH \\ OH \\ OH \end{cases} + 4\,H\,Cl.$$

$$2.\quad C\,(OH)_4 = C\,O\,(OH)_2 + H_2\,O, \text{ and}$$

$$3.\quad CO\,(OH)_2 = CO_2 + H_2\,O.$$

The action of alkalis differs from that of water for when carbon tetrachloride is treated with potassium or sodium hydroxide the stable potassium or sodium carbonate is produced.

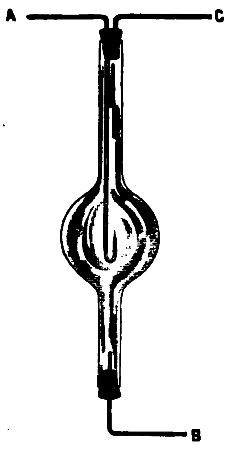


FIGURE 47.

Carbontetrabromide, $C\,Br_4$, and tetraiodide, $C\,I_4$, are also known; the former is a solid which melts at 91° and boils at 189.5°, the latter is a solid which breaks down into carbon and iodine when heated.

The two oxides of carbon are carbon monoxide, C O, and carbon dioxide, $C\,O_2$, only the latter acts like the anhydride of an acid.*

Carbon dioxide was formerly supposed to be the only oxide of carbon, for carbon monoxide even as recently as the beginning of this century was believed to be identical with hydrogen, or at least to contain hydrogen. Woodhouse, of Philadelphia, in the year 1800, first proved the combustible gas obtained by reducing metallic oxides with charcoal not to be hydrogen and demonstrated that it contained carbon, but carbon monoxide was not recognized as a combustible oxide of carbon until after the year 1802.

---

* A few cases in which carbon monoxide exhibits acidic properties are known. For instance, it unites with solid caustic potash when heated, forming potassium formate: $C\,O + K\,O\,H + C\,H\,O_2\,K.$

Carbon monoxide is produced by the incomplete combustion and also by the dry distillation of bituminus coal and of organic matter; for this reason it occurs in illuminating gas. Carbon monoxide is likewise always formed when reducible metallic oxides, such as those of iron or zinc, are heated with charcoal:

$$ZnO + C = Zn + CO.$$
$$Fe_2O_3 + 3\,C = 2\,Fe + 3\,CO.$$

indeed, the heating of metallic oxides with charcoal is a general method of preparing metals from their ores. These reactions are, however, like many others, reversible, so that carbon dioxide is reduced to carbon monoxide by metals such as iron or zinc, when these are heated to a high temperature. At 1300° carbon dioxide is partially decomposed into carbon monoxide and carbon. When steam is passed over red-hot charcoal, carbon-monoxide and hydrogen are produced:

$$H_2O + C = CO + 2\,H,$$

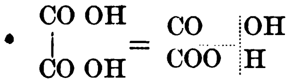
and the mixture of combustible gases so obtained, after being passed through volatile hydro-carbons, is quite extensively used as illuminating gas. Carbon dioxide can act like water in this respect, for when it is passed through a layer of hot coal, charcoal or coke, carbon monoxide results, as follows:

$$CO_2 + C = 2\,CO.$$

It is for this reason that the carbon dioxide produced by the free combustion of the coal just above the grate in a stove is changed to carbon monoxide by passing over the hot coals above. In many cases carbon monoxide acts as a reducing agent, for instance, the gas passed over red-hot ferric oxide reduces the latter to metallic iron:

$$Fe_2O_3 + 3\,CO = 2\,Fe + 3\,CO_2.$$

In order to prepare carbon monoxide for laboratory use advantage is taken of the decomposition of oxalic acid by heat or by means of concentrated sulphuric acid.* The acid breaks down as follows:



$$* \begin{matrix}\mathrm{CO\,OH}\\ | \\ \mathrm{CO\,OH}\end{matrix} = \begin{matrix}\mathrm{CO}\\ \mathrm{COO}\end{matrix}\left|\begin{matrix}\mathrm{OH}\\ \mathrm{H}\end{matrix}\right. \text{ or } C_2\,O_4\,H_2 = CO_2 + CO + H_2O.$$

The sulphuric acid which is added assists the operation by reason of its great tendency to take up water.[71] The carbon dioxide, formed simultaneously with carbon monoxide, can be removed by passing the mixture of gases through a solution of potassium hydroxide, by which means potassium carbonate is formed, while the carbon monoxide can be collected over water.

Carbon monoxide is a colorless gas which, when it is pure, has scarcely any odor. Its specific gravity, air = 1, is .968. Carbon monoxide is one of the gases which is with difficulty condensed to a liquid, it does not become fluid at —136° and under 150 atmospheres pressure, however, the application of a still greater cold changes it to a colorless liquid which boils at —190° under 760 m. m. pressure and which becomes solid at —199°. One volume of water dissolves about .2 of a volume of carbon monoxide, the gas is, however, quite soluble in a hydrochloric or ammoniacal solution of cuprous chloride.

Carbon monoxide burns readily in oxygen or in air; the product of the combustion is carbon dioxide:

$$CO + O = CO_2.$$

The pale blue flames observed above an anthracite coal-fire are caused by carbon monoxide.

The gas acts as a poison, replacing the oxygen which is chemically combined in the blood by an equal volume of carbon monoxide, each molecule of the latter substance must therefore take the place of a molecule of oxygen in oxyhæmoglobin, thereby destroying the oxidizing powers of the blood, for, as carbon monoxide forms a more stable compound with hæmoglobin than does oxygen, it is obvious that, once the carbon monoxide-hæmoglobin is formed, the latter compound cannot be broken up by oxygen. Blood which has been saturated with carbon monoxide retains its red color for a longer time than that which has been oxygenated.*

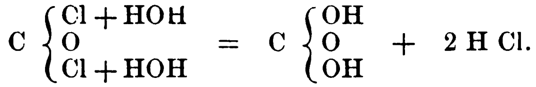
---

* This reaction is common to other dibasic organic acids.

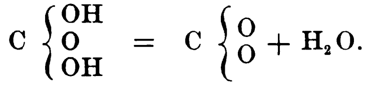
Carbon monoxide, when mixed with chlorine and placed in the sunlight, unites directly with that element to form carbonyl chloride:

$$CO + 2\,Cl = CO\,Cl_2;$$

this reaction being exactly like the similar one observed in the case of sulphur dioxide, (see page 141), water readily decomposes carbonyl chloride, forming hydrochloric acid and carbon dioxide. This reaction can be considered as taking place in two phases.

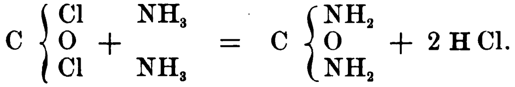
1. 

$$C\left\{\begin{matrix}Cl+HOH\\O\\Cl+HOH\end{matrix}\right. = C\left\{\begin{matrix}OH\\O\\OH\end{matrix}\right. + 2\,H\,Cl.$$

2. 

$$C\left\{\begin{matrix}OH\\O\\OH\end{matrix}\right. = C\left\{\begin{matrix}O\\O\end{matrix}\right. + H_2O.$$

The substance reacts in a similar way with ammonia, forming carbonyl diamide (urea) and hydrochloric acid.†



$$C\left\{\begin{matrix}Cl\\O\\Cl\end{matrix}\right. + \begin{matrix}NH_3\\ \\NH_3\end{matrix} = C\left\{\begin{matrix}NH_2\\O\\NH_2\end{matrix}\right. + 2\,H\,Cl.$$

Carbonic acid, H_2CO_3, can therefore be considered as carbonyl chloride in which two chlorine atoms have been replaced by hydroxyle groups, the acid itself, however, does not exist, it is only known as its anhydride CO_2, while from the above reaction it is evident that urea is carbonic acid in which two hydroxyle groups have been replaced by NH_2.

Carbon dioxide is of far greater importance than carbon monoxide. Its occurrence in the atmosphere and the manner and sources of its production were discussed on pages 161 and 162.

Phenomena by which carbon dioxide are produced were known in the earliest times, but the gas itself escaped observation. It was not until the close of the sixteenth century that a peculiar gas, which we now know to be carbon dioxide, was observed escaping from some mineral waters; Van Helmont (1577–1644) first distinguished this gas from others under the name of *gas sylvestre*, and showed that this substance was produced by the action of acids on alkalis or lime, by the burning of coals, and, in addition, was also formed during the processes of fermentation. Black in 1757 showed the difference between the so-called caustic alkalis (now known as hydroxides) and mild alkalis (carbonates) and found that a peculiar kind of air, (carbon dioxide) which he called fixed air, was expelled from the latter by the addition of acids. Lavoisier first explained the true nature of carbon dioxide and gave to it the name of *acide carbonique.*

---

*Carbon monoxide can readily be detected in the blood by means of the peculiarity of the absorption spectrum of blood saturated with that gas.

†The monovalent group NH_2 is called the amido group; see page 185.

Pure carbon dioxide can best be prepared by the addition of an an acid to some carbonate:

$$Na_2\,CO_3 + 2\,H\,Cl = 2\,Na\,Cl + H_2\,O + CO_2,$$
$$Ca\,CO_3 + 2\,H\,Cl = Ca\,Cl_2 + H_2\,O + CO_2,$$
$$Na_2\,CO_3 + H_2\,SO_4 = Na_2\,SO_4 + H_2\,O + CO_2.$$

Because carbonic acid is one of the weak acids and because it so readily breaks down into water and gaseous carbon dioxide (see page 274) it follows that almost any other acid will liberate carbon dioxide from the carbonates, so that the general formula:

$$M_2\,CO_3 + 2\,H\,X = 2\,M\,X + H_2\,O + CO_2$$

where M represents a univalent metal, and H X a monobasic acid, will hold good with very few exceptions.* The most convenient method of preparing carbon dioxide for laboratory use is by the action of dilute hydrochloric acid on the carbonate of calcium.[72]

Carbon dioxide is a colorless gas, which neither burns nor supports combustion. It has a specific gravity of 1.529, air=1, or 44, H=2, its molecular weight is therefore 44 and its formula CO_2. This formula is further sustained by the fact that there is no change in the volume of the gas when carbon burns in pure oxygen, so that each molecule of carbon dioxide must contain one molecule, or two atoms, of oxygen. Because carbon dioxide has such a high specific gravity it can be poured downward from any vessel containing it, and it is for this reason that carbon dioxide collects at the bottom of wells and mines into which the gas is escaping.[73] Cold and pressure combined condense carbon dioxide to a liquid which boils at—78.2°,* the vapor tension of fluid carbon dioxide is 36 atmospheres at 0° and 73 atmospheres at 30°, the critical point is 30.9°, above this temperature no pressure can convert the gas into a fluid. When carbon dioxide rapidly evaporates in a vacuum, the temperature sinks to 97°; the liquid, when allowed to escape from a small opening, condenses to a white, snow-like mass, the temperature of which, at atmospheric pressure, is -60°. Liquid carbon dioxide is colorless and has a specific gravity of .995 at 10°. Liquid carbon dioxide is extensively used in commercial operations, for instance in the manufacture of soda water, in fire extinguishers and in operations where the great pressure exerted by it can be used. A mixture of solid carbon dioxide and ether when placed under a vacuum can produce a cold of—110°.

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*Some few acids, like hydrocyanic acid, are unable to decompose carbonates, while some few carbonates which occur as minerals (for instance, dolomite) are not readily attacked by dilute acids. Quite a number of organic substances which act like acids are unable to decompose carbonates.

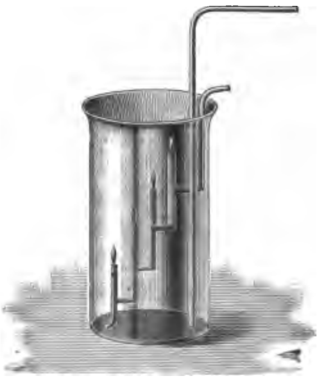


FIGURE 48.

Carbon dioxide is the anhydride of carbonic acid, but the latter substance is extremely unstable. It is probably formed as a white mass when the pressure is suddenly removed from carbon dioxide which, in the presence of water, has been nearly condensed to a liquid at 0°. There is no probability that water which is saturated with carbon dioxide at ordinary temperatures contains the acid $H_2 CO_3$ as such, for the solution behaves physically like an ordinary gas solution and not like that of an acid; on the other hand, the carbonates of the pronounced metals are extremely stable substances yet, with a diminution of the metallic nature of the salt-forming element, the carbonates become less stable until very weak bases like the oxide of aluminum or ferric oxide cannot react with carbonic acid at all.

---

* Doubtful.

The carbonates are all derived from a dibasic acid $H_2 CO_3$. The secondary carbonates, $M_2 CO_3$, are as a rule insoluble in water, only those of the alkali metals and of ammonium* dissolve, the other carbonates can therefore be obtained from these by precipitation with the soluble salt of some other metal, for example:

$$\underset{\text{Soluble.}}{Na_2 CO_3} + \underset{\text{Soluble.}}{Ba Cl_2} = \underset{\text{Insoluble.}}{Ba CO_3} + \underset{\text{Soluble.}}{2 Na Cl.}$$

The carbonates of the alkali metals can be fused without change, all other carbonates are more or less readily decomposed into carbon dioxide and the metallic oxide by heating, thus:

$$Ca CO_3 = Ca O + CO_2,$$

and this decomposition takes place the more readily the less basic the metallic oxide is, so that many carbonates are even decomposed on boiling with water. This increasing stability of the carbonates with the increase in the metallic character of the salt forming element is exactly parallel with the same gradation observed in the chlorides of the elements of the phosphorus family, (see page 211).

The primary carbonates, with the exception of those of the alkalis, exist only in aqueous solution, they can be obtained, where their existence is possible, by treating a solution of a secondary carbonate or even a finely divided insoluble secondary carbonate suspended in water, with carbon dioxide; they are unstable and are readily broken down by heat:

$$2 Na HCO_3 = Na_2 CO_3 + H_2 O + CO_2;$$

where they exist they are soluble. The solution of calcium carbonate in temporary hard water is caused by the formation of the primary calcium carbonate by means of the carbon dioxide contained in the air or added to the water by decaying substances:

$$Ca CO_3 + H_2 CO_3 = Ca (HCO_3)_2.$$

This soluble primary carbonate is decomposed when the water evaporates† or when it is heated. The temporary hard waters for this reason deposit their calcium carbonate as a white coating on the walls of the kettle in which they are boiled.

---

* Lithium carbonate is soluble with difficulty.

† Formation of stalactites.

Secondary carbonates, when soluble, have a strongly alkaline reaction, the primary ones are neutral.*

The following table gives a few of the most important naturally occurring carbonates:

Calcium carbonate, (Ca CO_3). } Massive varieties; chalk, limestone, marble.
Crystallized varieties; calcite (iceland spar), arragonite.
Calcium and magnesium carbonate, (Ca, Mg), CO_3, dolomite.
Ferrous carbonate; Fe CO_3, siderite.
Barium carbonate; Ba CO_3, witherite.
Strontium carbonate; Sr CO_3, strontianite.

The above carbonates are frequently found as isomorphous mixtures. The carbonates of lead, zinc and manganese are also found, as well as basic carbonates of copper, bismuth and zinc. Carbonates of sodium with more or less water of crystallization occur as soda ($Na_2\,CO_3 + 10\,H_2\,O$) and trona ($Na_4\,H_2\,[CO_3]_3\,3\,H_2\,O$).

The compound of carbon and sulphur which corresponds to $C\,O_2$ is $C\,S_2$, carbon disulphide. This liquid can be formed by heating carbon in sulphur vapor, so that the method of its production corresponds to that of carbon dioxide. Carbon disulphide is a colorless, mobile liquid, which, when pure, has a pleasant ethereal odor. Its specific gravity is 1.29, the specific gravity of its vapor is 2.626 (air = 1), it boils at 48° and is very little soluble in water. When gently warmed with the alkaline sulphides, carbon disulphide is dissolved while the salts of sulpho-acids are formed:

$$K_2\,S + C\,S_2 = K_2\,C\,S_3.$$

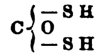
These salts of trithiocarbonic acid† correspond to those of carbonic acid, the oxygen atoms in the latter having been replaced by sulphur, on addition of acids to the salts, trithiocarbonic acid, $H_2\,C\,S_3$, separates as an oil:

$$K_2\,C\,S_3 + 2\,H\,Cl = H_2\,C\,S_3 + 2\,K\,Cl,$$

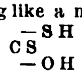
---

* They have no effect in litmus or turmeric paper but do have an alkaline reaction toward rosolic acid.

† The name *trithiocarbonic acid* is derived from Θεῖον sulphur, and the name thio-acids is frequently employed for sulpho-acids and thio compounds for sulpho compounds. An endeavor is made to establish the following distinction:—where sulphur is attached to carbon only, it is called *sulpho*, where it is attached to carbon on the one hand and a metal, or a group of elements acting like a metal, on the other, it is called *thio;* thus:



$C\left\{\begin{array}{l}-S\,H\\ O\\ -S\,H\end{array}\right.$ is *dithio*carbonic acid and



$C\,S\begin{array}{l}-S\,H\\ \\ -O\,H\end{array}$ is *sulphothio*carbonic acid. This nomenclature is, however, only logically carried out with the compounds of carbon.

but the thio acid so produced, although it is not as unstable as the corresponding oxy-acid, nevertheless, gradually breaks down as follows:

$$H_2\,C\,S_3 = H_2\,S + C\,S_2,$$

just as carbonic acid decomposes into water and carbon dioxide. These reactions of carbon disulphide remind us forcibly of the similar ones encountered with the sulphides of arsenic and antimony. (See pages 235, 245). A compound of carbon, oxygen and sulphur, having the formula $C\,O\,S$, which lies between the dioxide and sulphide of carbon, as well as acids derived from it, are also known.

CHAPTER XLI.

COMPOUNDS OF CARBON WITH NITROGEN, WITH NITROGEN AND HYDROGEN, AND WITH NITROGEN, OXYGEN AND HYDROGEN.

Only a very few of the more important of these compounds which can be strictly considered as belonging to the realm of inorganic chemistry can be briefly considered here. The most prominent of the substances to be discussed are derivatives of the monovalent group of elements cyanogen,* C N. This group can be attached to other elements or groups of elements in two ways, either by the element nitrogen, M N C, or by carbon, M C N; in the first case *isocyanides* are formed, in the second *true* cyanides (also called nitriles). Representatives of both classes of compounds are known.†

All nitrogen-bearing organic compounds, or, indeed, the nitrogenous coals derived from these, respectively yield the cyanides of sodium or potassium when heated with one of those metals; the cyanide of potassium is also formed when coal which contains nitrogen compounds is heated with common potash, by this means the greater quantity of the cyanide of potassium which finds commercial application is prepared. Free cyanogen can be formed by heating the cyanide of mercury to a dark red heat:

$$Hg\left\{\begin{matrix}C\,N\\C\,N\end{matrix}\right. = Hg + (C\,N)_2.$$

The group C N is as incapable of individual existence as is methyl, C H_3, two of the radicals therefore unite to form dicyanogen, C N — C N, just as methyl unites to form dimethyl.‡

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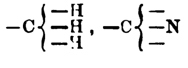
*From χύανος blue.

†The pupil must refer to some larger work on organic chemistry for the reactions which characterize the isocyanides.

‡ Cyanogen can be considered as methyl in which three atoms of hydrogen are replaced by one atom of trivalent nitrogen, viz:



$$-C\left\{\begin{matrix}-H\\-H\\-H\end{matrix}\right., \quad -C\left\{\begin{matrix}-\\-N\\-\end{matrix}\right.$$

Cyanogen is a colorless gas, extremely poisonous, with an irritating odor. Its specific gravity is 1.804, air = 1, or 51.9, H = 2, while the molecular weight of $(CN)_2$ is 52. The gas is quite soluble in water and is combustible, burning with a characteristic purple flame. It liquifies at —20.7° and becomes solid at —34.4°. Aqueous solutions of cyanogen gradually decompose.

Chemically, cyanogen greatly resembles the halogenes; the monovalent group CN when united with hydrogen forms hydrocyanic acid just as chlorine, similarly united, forms hydrochloric acid; furthermore, hydrogen, sodium or potassium will unite directly with cyanogen to form hydrocyanic acid, sodium cyanide or potassium cyanide, just as the same elements would unite with chlorine to form hydrochloric acid, sodium or potassium chloride. The group CN, cyanogen, is therefore a compound radical acting like a not metal and is chemically the opposite of the metal-like radical ammonium.

Hydrocyanic acid[*] is best prepared according to the general method by adding an acid to a cyanide.

$$2\,K\,CN + H_2\,SO_4 = 2\,H\,CN + K_2\,SO_4.\text{[†]}$$

When pure, hydrocyanic acid is a colorless, mobile liquid which boils at 26.5° and melts at —15°, it is without *acid reaction* toward litmus and has a peculiar odor somewhat resembling that of bitter almonds. It is intensely poisonous even when inhaled in small quantities, one drop placed on the tongue of a dog will cause instant death; the poison can also act through contact with abrasions of the skin. The acid mixes with water in all proportions and solutions of varying strength form the commercial prussic acid.

Two structural formulæ are possible for hydrocyanic acid, namely, $C = N — H$ and $H — C — N$, in the first one of these the hydrogen atom is attached to nitrogen, in the second to carbon; organic derivatives of both forms are known, the cyanides of the metals are most probably derivatives of the first form, CN H.[‡]

---

[*] Also called prussic acid because it is the source of prussian blue.

[†] The usual method is to decompose potassium ferrocyanide (see latter) with sulphuric acid.

[‡] The experiments which seem to indicate that cyanides are derived from both forms of hydrocyanic acid can easily be explained on the assumption that they are all derived from the first form.

Hydrocyanic acid is a very weak acid, the cyanides of the alkali metals and of barium, calcium or strontium are even decomposed by moist carbon dioxide, so that these substances, when in contact with the air, emit an odor of hydrocyanic acid. The cyanides of most of the heavy metals are insoluble, an exception to this rule is the cyanide of mercury; some of these cyanides are not readily decomposed by acids;* on the other hand, the alkaline cyanides, which are so readily decomposed by weak acids, are extremely stable when heated; they can even be fused without undergoing a chemical change. Almost all cyanides which are soluble in water are converted into so-called double cyanides when treated with the cyanides of the alkalis. Many of these double cyanides are stable, crystalline bodies which have the nature of chemical compounds; for example, ferrous cyanide when brought in contact with potassium cyanide forms a double cyanide of the formula $Fe\,(CN)_2 + 4\,K\,CN$.

$$\underset{\text{Ferrous cyanide}}{Fe\,(CN)_2} \quad + \quad \underset{\text{Potassium cyanide}}{4\,K\,CN} \quad = \quad \underset{\text{Potassium ferrocyanide.}}{K_4\,(CN)_6\,Fe.}$$

Potassium ferrocyanide bears no resemblance either to potassium cyanide or to ferrous cyanide, it is, indeed, the salt of a tolerably strong crystalline acid, hydroferrocyanic acid, $H_4\,(CN)_6\,Fe$, which latter can be prepared by the addition of strong hydrochloric acid to potassium ferrocyanide; the ferric salt of this acid, ferric ferrous cyanide, can be obtained from potassium ferrocyanide by adding a ferric salt:

$$3\,K_4\,(CN)_6\,Fe + 4\,Fe\,Cl_3 = Fe_4\,[(CN)_6\,Fe]_3 + 12\,K\,Cl.$$

This substance is the insoluble blue dye known as prussian blue. Ferric cyanide is also able to form a double salt with potassium, cyanide.

$$Fe\,(CN)_3 + 3\,K\,CN = K_3\,(CN)_6\,Fe,$$

and this substance, on addition of a ferrous salt, also forms an insoluble blue compound, Turnbull's blue.† The cyanides of other metals which are chemically closely allied to iron can form similar double cyanides; a larger work must be consulted in regard to the properties of those compounds. When cyanide of potassium is oxidized* it changes to the cyanate of potassium, CN OK. This oxidation is easily explained if we consider hydrocyanic acid as analogous to carbon monoxide:

---

* Mercury, silver and gold.

† Probably identical with prussian blue.

$$\begin{matrix}C{=}N{-}H, & \qquad & C{=}O, \\ \text{Hydrocyanic acid,} & \qquad & \text{Carbon monoxide;}\end{matrix}$$

for then it would naturally follow that the former would be oxidized as readily as the latter:

$$C{=}N{-}H + O = C\left\{\begin{matrix}N{-}H\\O\end{matrix}\right. \text{ and } C{=}O + O = C\left\{\begin{matrix}O\\O.\end{matrix}\right.$$

It seems highly probable, however, that the salts of this cyanic acid assume another form, namely, one in which the metallic atom is attached to oxygen:

$$C\left\{\begin{matrix}=N{-}H\\=O\end{matrix}\right. + \begin{matrix}O{-}H\\K\end{matrix} = C\left\{\begin{matrix}=N\\-O{-}K\end{matrix}\right. + HOH.\dagger$$

Such a difference between the structure of the free acid and of the salts derived from it seems not unlikely if the great tendency to unite with oxygen which is displayed by potassium or sodium is remembered. The acid having the formula CO NH is more accurately called isocyanic acid, and the one with the structure CN OH, cyanic acid. Isocyanic, or ordinary cyanic acid, is a very mobile, volatile liquid which is only stable below 0°, its odor resembles that of sulphur dioxide. A polymeric form of cyanic acid, $(CN\ OH)_3$, cyanuric acid, is also known, it is a solid substance.

The ammonium salt of cyanic acid, ammonium cyanate, on standing or more rapidly on heating, changes into urea, a substance of the greatest physiological importance:

$$CNO\ NH_4 = CO\ (NH_2)_2.$$

Urea can be considered as carbonic acid in which *both hydroxyles have been replaced by the amido group*, NH_2.

$$\begin{matrix}C\left\{\begin{matrix}OH\\O\\OH\end{matrix}\right. & \qquad & C\left\{\begin{matrix}-NH_2\\O\\-HH_2\end{matrix}\right. \\ \text{Carbonic acid.} & \qquad & \text{Urea.}\end{matrix}$$

---

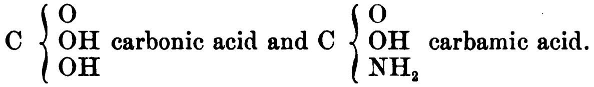
[*] This oxidation even takes place upon exposing potassium cyanide to the air.

[†] Organic derivatives obtained from the cyanates undoubtedly are derived from cyanic acid of the first formula, CO NH, but this fact does not seem to prove that the metal in the cyanates is attached to nitrogen.

On the other hand, when urea is heated it gives off ammonia and changes into the polymeric form of cyanic acid (cyanuric acid). Urea is a solid, white, crystalline substance which melts at 132°, and which occurs in many animal excreta, especially in the urine.

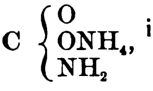
If *both* hydroxyle groups in carbonic acid can be replaced by the amido group, NH_2, it seems reasonable to suppose that a compound may exist in which only *one* of these has been substituted in this way, and indeed, such a substance is found in carbamic acid:.

$$CO_2\ HNH_2;$$



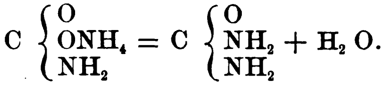
$$\mathrm{C}\left\{\begin{matrix}\mathrm{O}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}\right. \text{ carbonic acid and } \mathrm{C}\left\{\begin{matrix}\mathrm{O}\\ \mathrm{OH}\\ \mathrm{NH_2}\end{matrix}\right. \text{ carbamic acid.}$$

This acid is not known in the free state, but its ammonium salt,



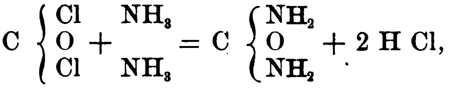
$$\mathrm{C}\left\{\begin{matrix}\mathrm{O}\\ \mathrm{ONH_4}\\ \mathrm{NH_2}\end{matrix}\right.,$$

is found in commercial carbonate of ammonia, on heating to 130° this compound changes into *urea:*



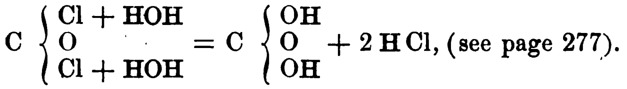
$$\mathrm{C}\left\{\begin{matrix}\mathrm{O}\\ \mathrm{ONH_4}\\ \mathrm{NH_2}\end{matrix}\right. = \mathrm{C}\left\{\begin{matrix}\mathrm{O}\\ \mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right. + H_2\,O.$$

Another interesting method by which urea can be formed is by means of the action of ammonia on carbonyl chloride:



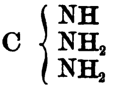
$$\mathrm{C}\left\{\begin{matrix}\mathrm{Cl} & \mathrm{NH_3}\\ \mathrm{O} + & \\ \mathrm{Cl} & \mathrm{NH_3}\end{matrix}\right. = \mathrm{C}\left\{\begin{matrix}\mathrm{NH_2}\\ \mathrm{O}\\ \mathrm{NH_2}\end{matrix}\right. + 2\,H\,Cl,$$

for this change is analogous to the reaction which takes place when water acts on the same substance:



$$\mathrm{C}\left\{\begin{matrix}\mathrm{Cl} + \mathrm{HOH}\\ \mathrm{O}\\ \mathrm{Cl} + \mathrm{HOH}\end{matrix}\right. = \mathrm{C}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{O}\\ \mathrm{OH}\end{matrix}\right. + 2\,H\,Cl, \text{ (see page 277).}$$

The oxygen atom in a formula weight of urea can be replaced by the divalent group $=NH$, and the resulting compound (guanidine), which has the formula

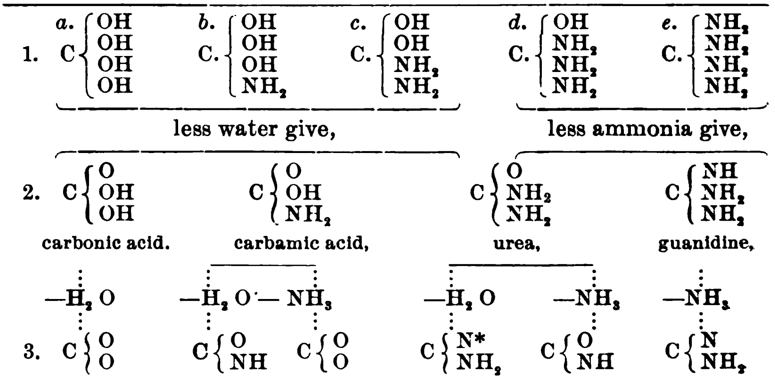


$$\mathrm{C}\left\{\begin{matrix}\mathrm{NH}\\ \mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right.$$

differs from urea but little in its character.

All of the foregoing compounds are extremely interesting from a theoretical standpoint because they illustrate the close resemblanec between the chemical nature of nitrogen and hydrogen united in the amido group and oxygen and hydrogen in hydroxyle, for the amido group can take part in the formation of compounds just as readily as the more familiar hydroxyle, and ammonia can, therefore, play much the same role as water in the reactions displayed by these carbon compounds. This similarity between nitrogen and oxygen compounds serves to illustrate forcibly the fact which has been repeatedly pointed out, namely, that no element is isolated in properties and chemical character and it should be the endeavor of every student of science to detect and understand the resemblances which are in reality present.

The connection between the compounds discussed in this and in the preceeding chapter will be more apparent from a study of the following table in which they have been placed side by side:



$$1.\quad a.\ C\begin{cases}OH\\OH\\OH\\OH\end{cases}\quad b.\ C.\begin{cases}OH\\OH\\OH\\NH_2\end{cases}\quad c.\ C.\begin{cases}OH\\OH\\NH_2\\NH_2\end{cases}\quad d.\ C.\begin{cases}OH\\NH_2\\NH_2\\NH_2\end{cases}\quad e.\ C.\begin{cases}NH_2\\NH_2\\NH_2\\NH_2\end{cases}$$

less water give, less ammonia give,

$$2.\quad C\begin{cases}O\\OH\\OH\end{cases}\quad C\begin{cases}O\\OH\\NH_2\end{cases}\quad C\begin{cases}O\\NH_2\\NH_2\end{cases}\quad C\begin{cases}NH\\NH_2\\NH_2\end{cases}$$

carbonic acid. carbamic acid, urea, guanidine,

$$-H_2O \qquad -H_2O - NH_3 \qquad -H_2O \qquad -NH_3 \qquad -NH_3$$

$$3.\quad C\begin{cases}O\\O\end{cases}\quad C\begin{cases}O\\NH\end{cases}\quad C\begin{cases}O\\O\end{cases}\quad C\begin{cases}N^*\\NH_2\end{cases}\quad C\begin{cases}O\\NH\end{cases}\quad C\begin{cases}N\\NH_2\end{cases}$$

carbon dioxide, cyanic acid, carbon dioxide, cyanamide. cyanic acid, cyanamide.

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* Cyanamide is a solid, melting at 40° and differing from urea by one molecule of water.

The hypothetical compounds *b*, *c*, *d*, *e* are supposed to be derived from the hypothetical normal carbonic acid (*a*) by replacing hydroxyle groups by amido groups (OH by NH_2). In this table the hydroxyle group is considered as analogous to the amido group and of equal valence and the group NH (imide group) as analogous to a divalent oxygen atom. Of the compounds under (2) carbonic acid and carbamic acid are only known in their derivatives.

CHAPTER XLII.

SILICON, THE COMPOUNDS OF SILICON WITH HYDROGEN AND WITH THE HALOGENES.

Silicon, symbol Si, atomic weight 28.4, specific gravity of solid (graphitoidal) 2.49.

Silicon never occurs in nature as the uncombined element, but silicon compounds are among the most important and widely distributed constituents of the crust of the earth, the primitive crystalline rocks are in greater part either silicon dioxide or else salts of the various silicic acids so that, it has been estimated, 27.2 per cent. of the globe (excluding the atmosphere) consists of silicon. Despite the abundance of silicon compounds the element itself was not discovered until 1823, in which year it was isolated by Berzelius.

Silicon is best prepared by the reduction of some of the halogene compounds of the element by means of sodium or potassium; for instance, by passing the vapors of the tetrachloride of silicon over heated sodium:

$$Si\,Cl_4 + 4\,Na = Si + 4\,Na\,Cl.$$

The element so prepared is an amorphous brown powder, which does not conduct electricity; it is readily ignited in the air, burning to form silicon dioxide. Silicon is produced when potassium or sodium fluosilicates* are fused with alumimium; the alumimium, uniting with the fluorine, in part forms aluminium fluoride, while the unchanged, molten metal dissolves the silicon which is liberated; when the mass is cooled a portion of the silicon separates in needle-shaped crystals. † Silicon crystallizes in greyish black, regular octahedra which have a metallic lustre. The silicon which is formed from molten iron or zinc may also have the appearance of graphite, although the crystalline form is, apparently, the same as that of the needle like crystals; graphitoidal silicon has a specific gravity of 2.49; crystallized silicon conduct electricity readily and cannot be ignited in the air. When heated to a high white heat, silicon can be fused and even cast into sticks, when cooled it solidifies to form a mass which somewhat resembles a piece of pure crystalline graphite. The amorphous and crystalline varieties of silicon remind us of the similar forms displayed by carbon.

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* $K_2\,Si\,F_6$ or $Na_2\,Si\,F_6$, salts of fluosilicic acid, $H_2\,Si\,F_6$.

† Melted zinc or iron can also dissolve silicon, when they cool, the silicon separates in crystals; as silicon is formed from silicon dioxide, carbon and iron at a high heat it follows that ordinary pig iron must contain silicon.

Only one compound of silicon and hydrogen, silicon hydride, $Si\,H_4$, is known. This substance bears a great resemblance to the corresponding compound in the nitrogen family, namely to phosphine, for it takes fire spontaneously when brought into the air and it is formed by the action of an acid on magnesium silicide, just as phosphine is produced from calcium phosphide. The preparation of pure silicon hydride is a difficult process. Silicon hydride is a colorless gas which, when pure, does not take fire spontaneously, but which has such a low kindling temperature that it can readily be ignited by a warm glass rod, the gas is liquified at —11° by a pressure of 80 atmospheres. Silicon hydride is, of course, readily decomposed by chlorine or bromine, and it resembles hydrogen sulphide and phosphine by producing precipitates with quite a number of metallic salts.

The few compounds of silicon and the halogenes which exist are of the same general formula as the corresponding compounds of carbon; silicochloroform, $Si\,H\,Cl_3$, corresponding to ordinary chloroform, $C\,H\,Cl_3$, and silicon tetrachloride, $Si\,Cl_4$, corresponding to $C\,Cl_4$ serve to illustrate this resemblance. The halogene compounds of silicon are all unstable bodies which are decomposed by water to form silicic acid and the corresponding halhydric acid:

$$Si\,Cl_4 + 3\,H_2\,O = Si\,O_3\,H_2 + 4\,H\,Cl.$$

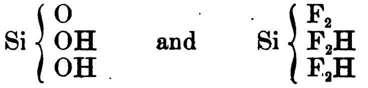
The most important halogene compound of silicon is undoubtedly the tetrafluoride, $Si\,F_4$. This substance can readily be produced by the action of hydrofluoric acid on silicon dioxide:

$$Si\,O_2 + 4\,H\,F = Si\,F_4 + 2\,H_2\,O.$$

In this reaction the silicon dioxide is a base, for it yields a salt and water when brought in contact with an acid. Silicon tetrafluoride is a colorless gas which fumes strongly in the air, because when in contact with water vapor it decomposes and forms silicic acid. At a temperature of —100° silicon tetrafluoride is converted into a white solid. The specific gravity of the vapor, air = 1, is 3.6, a number which would agree with a calculated molecular weight of 103.4, so that according to this the molecule of silicon tetrafluoride is $Si\ F_4$. As silicon tetrafluoride is readily produced by the action of hydrofluoric acid on silicon dioxide, it follows that the acid will attack glass, for that substance contains a large proportion of silicon dioxide.[74] Water instantly decomposes silicon tetrafluoride, forming silicic acid and fluosilicic acid:

$$2\ Si\ F_4 + 3\ H_2\ O = H_2\ Si\ O_3 + Si\ F_6\ H_2 + 2\ HF.$$

Fluosilicic acid is especially interesting because it shows the chemistry of fluorine to us in an entirely new light, for if we compare the following two formulæ:



$$Si\begin{cases} O \\ OH \\ OH \end{cases} \quad \text{and} \quad Si\begin{cases} F_2 \\ F_2H \\ F_2H \end{cases}$$

silicic acid and fluosilicic acid;

we see that fluosilicic acid is constructed similarly to silicic acid, but with this difference; for each oxygen atom in silicic acid we have two fluorine atoms in fluosilicic acid. *Two fluorine atoms* in some chemical compounds are therefore able to take the place of *one* oxygen atom without materially altering the chemical nature of those compounds. Substances which are constructed in a manner similar to fluosilicic acid are not infrequent, but, as their resemblance to oxygen compounds is not generally so marked as in the case under discussion, their true nature is often misunderstood and concealed under the names of double salts (see aluminium).* The wider the range of our acquaintance with chemical compounds becomes the more do we see that the most various substances, which may or may not contain oxygen, can act as acids, provided only they contain hydrogen, which hydrogen is attached to a not metallic element or group of elements and which hydrogen can be replaced by metals to form salts (see page 71). The reason for the salt formation is found in the simple fact that the salts produced by the replacement of the acid hydrogen possess less chemical energy than do the acids themselves, so that the reactions by which these salts are formed are exothermic. One consideration forces itself upon us when we study the structural formula of fluosilicic acid, and that is the impossibility of maintaining the theory of the constant monovalence of fluorine, for, unless we wish to take the untenable position that fluosilicic acid is a compound formed of finished molecules of silicon fluoride and hydrofluoric acid, is a so-called "molecular compound," we must look upon the fluorine atoms as being divalent in fluosilicic acid:

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* The acid derived from ferrocyanic acid, $H_4\ Fe\ (CN)_6$, may be cited as an instance where a complex compound containing hydrogen and in which cyanogen has taken the place of oxygen, can act as an acid.

$$\mathrm{Si}\left\{\begin{array}{l} \mathrm{F—F} \\ \mathrm{F—F} \\ \mathrm{F—F—H} \\ \mathrm{F—F—H} \end{array}\right.$$

Even if we call this acid a molecular compound ($Si\ F_4$, 2 HF) such a supposition does not help matters in the least, for then we must regard $Si\ F_4$ and HF as still having chemical affinity at their disposal, which supposition is contrary to the theory that silicon is only tetravalent and fluorine only monovalent, for then neither of these compounds should be capable of further union after $Si\ F_4$ and HF have been formed. So long, therefore, as our present theories of valence are maintained we must regard fluorine as being both uni and bivalent. This conclusion is strengthened by the fact that the specific gravity of hydrofluoric acid shows that substance to be $H_2\ F_2$.

Fluosilicic acid is only known in solution, when evaporated beyond a certain concentration it breaks down into silicon fluoride and hydrofluoric acid, much as ordinary silicic acid does into silicon dioxide and water. A similar change takes place with the fluosilicates, for these salts, when heated, break down into silicon tetrafluoride and the fluoride of the metal entering into the salt:

$$Si\ F_6\ K_2 = Si\ F_4 + 2\ KF.$$

Almost all of the silicofluorides are soluble in water, the fluosilicate of potassium is, however, nearly insoluble and, as almost all potassium salts are dissolved by water, it is evident that fluosilicic acid is a very welcome reagent for the detection of potassium compounds in solution.

Silicon forms but one oxide, the dioxide $Si\ O_2$. This substance occurs in three forms:—crystalline, cryptocrystalline, and amorphous. Crystallized silicon dioxide is dimorphous, being found as quartz* and as tridymite.† The quartz crystals are often colored more or less by impurities, when the color so produced is purple or bluish violet the crystal is called amethyst. The crystallized variety of quartz frequently occurs in large masses, displaying no crystalline faces, while smaller fragments of the mineral are found as a constituent of the granitic rocks. The cryptocrystalline ‡ varieties of quartz show the greatest diversity of color and appearance; they generally contain more or less water and are more readily acted on by hydrofluoric acid than the crystallized varieties. Examples of cryptocrystalline quartz are chalcedony, carnelian, agate, onyx and flint. Sea sand consists, for the most part, of quartz finely ground by the action of the water. Amorphous silicon dioxide can be prepared by the addition of an acid to a soluble silicate:

$$\underset{\text{Sodium silicate.}}{Na_2\ Si\ O_3} + 2\ H\ Cl = \underset{\text{Silicic acid.}}{H_2\ Si\ O_3} + 2\ Na\ Cl;$$

and by then heating the silicic acid until all water is expelled; the silicon dioxide formed in this way is a white, impalpable powder which can be readily dissolved in alkalis; when heated to a high white heat this variety of the dioxide becomes crystalline and can then no longer be dissolved by cold alkalis.

The two simplest theoretical hydrates of silicon dioxide are ortho-silicic acid, $Si\ (O\ H)_4$, and meta-silicic acid, $Si\ O_3\ H_2$; neither of these acids are known with certainty, but a solution which probably contains ortho-silicic acid can be obtained by the following means:—By adding cold dilute hydrochloric acid to a very dilute cold solution of sodium silicate the following reaction presumably takes place:

$$Na_2\ Si\ O_3 + 2\ H\ Cl = H_2\ Si\ O_3 + 2\ Na\ Cl;$$

the meta-silicic acid so formed then unites with water to form ortho-silicic acid:

$$H_2\ Si\ O_3 + H_2\ O = H_4\ Si\ O_4.$$

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* Hexagonal, tetartohedral; combinations of pyramid and prism.

† Asymmetric.

‡ Varieties of crystalline minerals in which the crystals are so small as not to be detected by the eye are called cryptocrystalline. Such rocks are frequently erroneously termed amorphous.

Under the conditions of the reaction there is no separation of insoluble silicic acid, as there is when the solutions are more concentrated or when they are heated. If the clear liquid containing sodium chloride and silicic acid is put in a vessel the bottom of which is formed of a membrane such as parchment, and this vessel is then placed in pure water, the sodium chloride will pass out into the water, while the silicic acid will remain behind in the solution. The process by which this separation takes place is *osmosis* and the silicic acid is said to be separated by *dialysis;* substances which are able to pass through such a membrane are called crystalloids, those which cannot pass through, colloids. As the process of osmosis is one of extreme importance in animal and plant life, a brief discussion of some of the principal facts which have been learned regarding it may not be out of place here.*

When a layer of water is carefully poured over any aqueous solution, the two liquids will not remain in this condition, for diffusion will take place just as it does between layers of different gases (see page 32), so that the solution will begin to rise in a direction contrary to the force of gravity and will finally completely mix with the pure water, the motion only ceasing when the substance in solution is uniformly distributed throughout the mass of water. This motion can be arrested by placing a septum between the water and the solution and if this septum is of such a material as to allow water to pass through but not the dissolved substance, and if furthermore the septum is in the shape of a cell which can be covered by an air-tight cap which is so constructed that it can be connected with a manometer by a glass tube, an increase of pressure will be observed in the interior of the cell, because the water will force its way in while the substance in solution cannot escape. Now a remarkable fact is observed in regard to this pressure, for if the temperature is kept constant the pressure will be *proportional to the strength of the solution;* thus with a solution of sugar the following pressures were observed:

A 1 per cent. solution gave a pressure of 535 m. m.
" 2 " " " " " " " 1016 " "
" 4 " " " " " " " 2082 " "

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* See Ostwald, Outlines of General Chemistry (Walker), for a more complete description of this topic.

These observed pressures in millimeters are nearly in the proportion of 1:2:4. This law of osmotic pressure, which is true of all dissolved substances is exactly like that regulating the pressure of gases, for these are also proportional to the densities (i. e. concentrations). It has further been observed that *temperature* has the same influence on osmotic pressure as it has on the pressure of gases, for the pressure increases proportionally to the absolute temperature and in the same ratio for all dissolved substances. The increase in pressure for each degree of temperature is $\frac{1}{273}$ *, the same fraction obtained as an increase for each degree in the pressure of gases which are kept at constant volume. The relation* for osmotic pressure may therefore be expressed in the same way as for gases. If we know the osmotic pressure (P°) at 0°, then at t° it will be $P^\circ + P^\circ .00367\ t = P^\circ (1 + .00367\ t)$ (see pages 167, 168). The osmotic pressure of a substance in solution has the same value as the pressure that substance would exert were it contained as a gas in the same volume as is occupied by the solution. It seems reasonable to suppose, therefore, that, as the same laws which govern the pressures of gases hold good with osmotic pressure, the substances which are contained in solution are present in such solution in the same condition as they occur in gases, i. e., as the individual molecules.

The membranes through which the various fluids in living organisms must find their way by osmosis, act on the same principle as the septa which are artificially prepared, and, as the same increase of temperature causes a like increase of osmotic pressure in all fluids, it follows that solutions which are in osmotic equilibrium between the contents of a living cell and the liquid without at any given temperature, say 0°, are also in equilibrium at 38°.

When the solution containing dialized silicic acid is evaporated the acid congeals to a gelatinous mass, which is then no longer soluble in water, and when this is separated and dried the remaining amorphous powder has the formula, approximately, of H_2SiO_3, this, when heated, loses water and forms amorphous silicon dioxide.

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* Exactly .00367.

The silicates are either orthosilicates, $M_4\,Si\,O_4$, or metasilicates $M_2\,Si\,O_3$, or they are derived from more complicated silicic acids which, according to the number of silicon atoms in their formula weights are called di, tri or, in general, polysilicates. All of these salts have numerous representatives in the mineral deposits of the earth. The formulæ of a few of these are given in the following tabular statement:

Orthosilicates:

$$\text{Acid, Si}\left\{\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}.\end{array}\right.$$

Olivin, $Mg_2\,Si\,O_4$, $Fe_2\,Si\,O_4$.
Garnet, $Ca_3\,Fe_2\,(Si\,O_4)_3$.*
Mica, the various forms of this mineral are complicated orthosiliates.

Metasilicates:

$$\text{Acid, Si}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{OH}\\ \mathrm{OH}\end{array}\right.$$

Wollastonite, $Ca\,Si\,O_3$.
Leucite, $K\,Al\,(Si\,O_3)_2$.
Beryll, $Be_3\,Al_2\,(Si\,O_3)_6$.
Related to wollastonite, but of more complicated structure, are the important minerals hornblende and augite.

Disilicic acid is formed by the separation of one molecule of water from two formula weights of metasilicic acid, just as disulphuric acid is derived from two of sulphuric (page 150).

$$\mathrm{Si}\left\{\begin{array}{lcl}\mathrm{O} & & \mathrm{O}\\ \mathrm{OH} & + & \mathrm{HO}\\ \mathrm{OH} & & \mathrm{HO}\end{array}\right\}\mathrm{Si} = \mathrm{Si}\left\{\begin{array}{lcl}\mathrm{O} & & \mathrm{O}\\ \mathrm{OH} & & \mathrm{HO}\\ & -\mathrm{O}- & \end{array}\right\}\mathrm{Si}.$$

Only two or three examples of disilicates are known. Trisilicic acid is formed by separating four molecules of water from three formula weights of $Si\,(OH)_4$; $3\,Si\,(OH)_4 - 4H_2\,O = Si_3\,O_8\,H_4$.

Trisilicates:

$$\text{Acid, }\begin{array}{r}\\ \mathrm{Si}\\ \\ \\ \mathrm{Si}\\ \\ \\ \mathrm{Si}\end{array}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{OH}\\ \mathrm{O}\\ \mathrm{OH}\\ \mathrm{OH}\\ \mathrm{O}\\ \mathrm{OH}\\ \mathrm{O}\end{array}\right.$$

Orthoclase, (feldspar) $K\,Al\,Si_3\,O_8$.
Oligoclase (soda, lime feldspar) $Na\,Al\,(Si_3\,O_8)$, $Ca\,Al\,(Al\,Si_2)\,O_8$.
In the important group of minerals known as feldspars it not infrequently happens that a portion of the silicon is replaced by aluminium, this is seen in the formula of oligoclase.

The quantitative composition of the silicates shows that every one of them can be considered as derived from one of the above mentioned acids. A number of basic and acid silicates also exist. Among acid silicates, kaolin (clay) $H_2\ Al_2\ (Si\ O_4)_2 + H_2\ O$, may be mentioned.

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* Of the twelve hydrogen atoms in three formula weights of orthosilic acid, six are replaced by trivalent iron and six by bivalent calcium. In this silicate, and in others, two or more formula weights of the acid are united by an atom of a polyvalent element replacing hydrogen atoms which belong, in part, to one and in part to another formula weight of the acid, a simple example of such a case we have encountered in the formula of the tertiary phosphate of calcium, $Ca_3\,(PO_4)_2$, (seepage 220).

The silicates are such extremely important minerals, their composition is so varied and their distribution so far reaching, that the study of their structure forms one of the most important branches of modern mineralogy. All silicates, excepting those of the alkali metals, are insoluble in water.

CHAPTER XLIII.

GERMANIUM AND ITS COMPOUNDS.

Germanium, symbol Ge, atomic weight 72.3.

This element was discovered in the year 1886, by the German chemist, Clemens Winckler, and is especially interesting from the fact that it is one of the elements the existence of which was predicted before its discovery. This prediction was based upon the fact that, when the elements are arranged in the order of their atomic weights (page 16) an unfilled gap was found to exist between gallium (atomic weight 69) and arsenic (atomic weight 75), which gap, as the nature of the then known elements showed, should be filled by a representative of the carbon family (see table of the periodic system). The element was discovered in a silver ore which was formerly confounded with silver sulphide (argentite) and which has the formula $3\ Ag_2\ S,\ Ge\ S_2$. The isolation of the element is a very complicated process.

Germanium, owing to its higher atomic weight, must be much more metallic in its nature than silicon and, indeed, this difference in its character is shown by the non existence of a hydrogen compound of the element. The metal has a brilliant metallic lustre, and like its fellows, carbon and silicon, it crystallizes in crystals belonging to the regular system. Its specific gravity is 5.46, and its melting point less than that of silver (954°). The metal is neither malleable nor ductile, it is quite brittle and can be readily pounded to a powder, in this respect it resembles arsenic. When heated to a high heat in the air, the metal, after fusing, oxidizes to form the oxide $Ge\ O_2$. Germanium does not dissolve in hydrochloric acid, it is oxidized to $Ge\ O_2$ by nitric acid or aqua regia. Hot and concentrated sulphuric acid dissolves it to form the sulphate, while the acid is itself reduced to sulphur dioxide (see page 133).

Germanium combines with all of the halogenes to form compounds of the general formula $Ge\,R_4$, where R represents an atom of any halogene. Germanium tetrachloride, formed by passing chlorine over heated germanium, is a colorless liquid which very much resembles the corresponding chloride of silicon, $Si\,Cl_4$; it is decomposed by water and boils at 86°; the specific gravity of its vapor (between 300° and 740°) is 7.43, this, $H = 2$, is 213.9; the calculated molecular weight for $Ge\,Cl_4$ is 214 ($Ge = 72.3$, $4\,Cl = 142$) it follows from this that the formula of the chloride of germanium corresponds to that of silicon or carbon, and that the maximum atomic weight of germanium is 72.3 (see page 69). As, before the discovery of germanium, no element was known to exist having an atomic weight between that of gallium (69) and arsenic (75), and as an element belonging to the carbon family and having an atomic weight of approximately 72 would evidently find a fitting place in the system obtained by arranging the elements in the order of their atomic weights, therefore, the gravimetric quantity of germanium, (72.3), which unites with 142 (or 4x 35.5) parts by weight of chlorine is more than probably the correct atomic weight of the element in question. If, at any time, a compound of germanium should be discovered which, with a known molecular weight, should contain less than 72.3 parts by weight of that element, then the atomic weight which is at present accepted will have to be abandoned. A compound of germanium and chlorine, $Ge\,Cl_2$, corresponding to stannous chloride, $Sn\,Cl_2$, has also been observed. The other halogene compounds of the element need not be described, although the existence of a germanium chloroform, $Ge\,H\,Cl_3$, a compound corresponding to chloroform, $CH\,Cl_3$ and to silicon chloroform, $Si\,H\,Cl_3$, should be emphasized as showing the relationship between germanium and the preceding elements of this family.

Germanium forms two oxides, $Ge\,O_2$ and $Ge\,O$. The former is produced either by burning the powdered element in a stream of oxygen, by oxidizing it with nitric acid or by decomposing the chloride with water. It is a white powder, somewhat soluble in water, the solution probably containing the hydroxide $H_2\,Ge\,O_3$, corresponding to metasilicic acid, $H_2\,Si\,O_3$. Germanium dioxide acts as a weak acidic anhydride, dissolving in the hydroxides of the alkali metals; it has no basic properties. The second oxide, $Ge\ O$, is an unstable substance which oxidizes in the air, has a hydroxide, $Ge\ (O\ H)_2$, derived from it, and is weakly basic in its character. It is a powerful reducing agent.

Two sulphides of germanium, $Ge\ S_2$ and $Ge\ S$, are known. These correspond to the sulphides of tin. The disulphide, $Ge\ S_2$, dissolves in the sulphides of the alkali metals to form sulpho-salts, it therefore has the character of an acidic anhydride and resembles the sulphides of arsenic, antimony, tin and carbon.

CHAPTER XLIV.

TIN AND ITS COMPOUNDS.

Tin: Symbol Sn; Atomic weight, 119.

Tin, the third element of the carbon family, has its metallic properties so decidedly pronounced that, disregarding its many resemblances to the not-metals, it is generally classed with the metals. In reality it bears about the same relation to metals and not-metals as antimony does; however, both of its oxides, $Sn\ O$ and $Sn\ O_2$, have basic properties and, furthermore, tin cannot form a hydrogen compound, but, on the other hand, both oxides when in contact with strong bases, can act like acidic anhydrides.

The time of the discovery of tin is not known. A knowledge of the metal has been attributed to the Hebrews, Greeks and Phœnicians, but no certainty exists as to this. Undoubtedly, Pliny distinctly mentions tin under the name of plumbum candidum, and moreover the metal was used by the Romans for covering iron in order to keep that metal from rusting. The term stannum dates from the fourth century.

Tin is one of the comparatively rare elements, and its occurrence in the free state as a mineral is somewhat doubtful. It is chiefly found as cassiterite or tin stone, which is the crystallized dioxide, $Sn\ O_2$; this substance is deposited in crystals and in the massive form in veins traversing granite, gneiss and mica schist in Cornwall and Devonshire, in Bohemia, Saxony, New South Wales, and Queensland. Some tin has also been discovered in the United States. An impure sulphide of tin, stannnite, $Sn\ S_2$, occasionally appears in mineral deposits.

The tin of commerce is exclusively prepared from tin stone, which is first crushed and washed and then heated with charcoal according to the usual metallurgical process (see page 238). The tin which melts and is collected at the bottom of the furnace is generally quite impure, for it contains copper, iron, arsenic, antimony and lead. These foreign substances are for the most part removed by heating the crude tin to a temperature just above its melting point and then allowing the pure metal to run off from its higher melting alloys.

Tin is nearly silver-white, with a metallic lustre; it is scarcely corroded when exposed to the air; it is soft and can be hammered and rolled into thin sheets (tin foil); its specific gravity is 7.3; it melts at 230° and evaporates at a temperature between 1600° and 1700°. The metal has a great tendency toward crystallization, either when it is separated from its compounds* or when it congeals after fusion. The element, like carbon, is dimorphous, occurring both in tetragonal and in rhombic crystals. If block tin is cooled to a very low temperature, or even if it is allowed to stand for a long time, it undergoes a peculiar change into a greyish powder, which can will reassume a metallic appearance only upon being fused. This amorphous form of tin would correspond to amorphous carbon or silicon. Ordinary tin, cast into forms, assumes a crystalline structure; if a stick formed of the metal is bent, a peculiar crepitation is observed, and if the operation is rapidly repeated several times, the piece of tin will become quite hot at the place of bending; both the noise and the heat are caused by the friction of the minute crystals one upon the other.

Tin is attacked by acids with considerable ease; hydrochloric acid dissolves it to form stannous chloride:

$$Sn + 2\,H\,Cl = Sn\,Cl_2 + 2\,H;$$

and in this way the element shows its metallic nature, that this is not very pronounced, however, is shown by the fact that the reaction between tin and hydrochloric acid takes place much more slowly than it does between the same acid and iron or zinc. Hot and concentrated sulphuric acid dissolves tin to form stannous sulphide,

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* By electrolysis of stannous chloride or by placing a piece of zinc in a solution of stannous chloride, the zinc then takes the place of tin in the salt:

$$Zn + Sn\,Cl_2 = Zn\,Cl_2 + Sn.$$

Such substitutions of one metal for another in salts are quite frequently met with but are not surprising if we compare salts with acids, for, as we know, zinc can readily replace hydrogen in hydrogen chloride and why not tin in stannous chloride? The only essential is that $Sn\,Cl_2$ should have more chemical energy than $Zn\,Cl_2$ and that heat should be given off in the reaction.

while the acid is reduced to sulphur dioxide (see page 133). Cold and dilute nitric acid dissolves tin without any evolution of gas; the tin forms stannous nitrate, while the nitric acid is reduced to ammonia (page 198 [a]) as is represented by the following equation:

$$4\,Sn + 10\,H\,N\,O_3 = 4\,Sn\,(N\,O_3)_2 + N\,H_4\,N\,O_3 + 3\,H_2\,O.$$

On the other hand, hot and concentrated nitric acid oxidizes tin to insoluble metastannic acid, $H_2\,Sn\,O_3$, and is itself reduced to some of the lower oxides of nitrogen (page 198 [b]).* Tin shows its relationship to the not-metals by dissolving in soluble alkaline hydroxides to form salts of stannic acid, $M_2\,Sn\,O_3$.

Tin forms two series of compounds with the halogenes; the first of these, with the general formula $Sn\,X_2$, where X represents any halogene, can be formed, as are the salts of other metals, by dissolving the corresponding oxide in halhydric acids:

$$Sn\,O + 2\,H\,X = Sn\,X_2 + H_2\,O,$$

while the compounds $Sn\,X_2$ can be converted into those of the second series, $Sn\,X_4$, by the addition of the corresponding halogene. The two chlorides of tin, $Sn\,Cl_2$, stannous chloride, and $Sn\,Cl_4$, stannic chloride, (see pages 24 and 25) are the most important of these halogene compounds.

Stannous chloride, $Sn\,Cl_2$, can be formed by dissolving tin or stannous oxide, Sn O, in hydrochloric acid; when anhydrous it is a crystalline substance which melts at 250° and boils at 606°; its vapor density was formerly supposed to correspond to a molecular weight calculated from the formula $Sn_2\,Cl_4$, but later investigations have shown that no definite specific gravity can be assigned to it. Stannous chloride dissolves in small quantities of water without change; an excess of the solvent, however, partially converts it into an insoluble basic chloride (see page 242):

$$Sn\begin{cases}Cl + H\,O\,H \\ Cl\end{cases} = Sn\begin{cases}OH \\ Cl\end{cases} + H\,Cl.$$

Stannous chloride is a powerful reducing agent; when exposed to the air it absorbs oxygen and changes into a mixture of stannic chloride and the basic chloride just mentioned. Stannous chloride instantly reduces mercuric chloride to mercurous chloride:

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* Compare with antimony page 239.

$$2\,\mathrm{Hg\,Cl_2} + \mathrm{Sn\,Cl_2} = \mathrm{Sn\,Cl_4} + 2\,\mathrm{Hg\,Cl},^*$$

and the mercurous chloride, by further action, is even finally changed to mercury. Ferric chloride is reduced to ferrous chloride by stannous chloride:

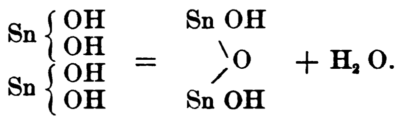
$$2\,\mathrm{Fe\,Cl_3} + \mathrm{Sn\,Cl_2} = \mathrm{Sn\,Cl_4} + 2\,\mathrm{Fe\,Cl_2},$$

while arsenic trioxide is reduced to metallic arsenic by the same substance, the compound of tin being in this case oxidized to stannic acid.

When alkaline hydroxides are added to a solution of stannous chloride, insoluble stannous hydroxide is at first precipitated:

$$\mathrm{Sn\,Cl_2} + 2\,\mathrm{KOH} = \mathrm{Sn\,(OH)_2} + 2\,\mathrm{K\,Cl},$$

but this substance, because it presents in a slight degree the character of an acid, is dissolved by an excess of the alkaline solution to form stannites, which are salts of a stannous acid having the formula $\mathrm{H_2\,Sn_2\,O_3}$, formed, as are a number of acids which we have already discussed, by the separation of one molecule of water from two formula weights of the hydroxide:



$$\begin{matrix}\mathrm{Sn}\left\{\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}\right.\\\mathrm{Sn}\left\{\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}\right.\end{matrix} = \begin{matrix}\mathrm{Sn\,OH}\\ \rangle\mathrm{O}\\ \mathrm{Sn\,OH}\end{matrix} + \mathrm{H_2\,O}.$$

The potassium compound, formed by dissolving stannous hydroxide in an excess of potassium hydroxide, therefore has the formula $\mathrm{K_2\,Sn_2\,O_3}$; this salt, when heated, breaks down into tin and potassium stannate:

$$\mathrm{Sn_2\,O_3\,K_2} = \mathrm{Sn\,O_3\,K_2} + \mathrm{Sn}.^\dagger$$

Stannic chloride can be formed from stannous chloride by heating the latter substance and then passing dry chlorine over it. It is a colorless liquid which fumes in the air and which boils at 120°, it greedily absorbs moisture and then produces crystals having the formula $Sn\ Cl_4 + 3\ H_2 O$. Stannic chloride forms a series of double salts with the chlorides of the alkali metals,* these double salts have the general formula $Sn\ Cl_6\ M_2$, where M represents an atom of an alkali metal, they therefore correspond to the silico-fluorides, $Si\ F_6\ M_2$, (see page 292) which we looked upon as salts of fluosilicic acid $H_2\ Si\ F_6$, there is consequently no reason why the conclusions regarding the nature of fluorine in the fluosilicates should not be equally applicable in the case of chlorine in these compounds of tin, indeed, a substance $H_2\ Sn\ Cl_6$, which must be considered as the acid from which these double salts are derived, has in all probability been isolated.

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* For this reason stannous chloride is used as a reagent for soluble salts of mercury, for as mercurous chloride is insoluble in water, a precipitate of the latter is formed when stannous chloride is added to a solution containing mercury.

† See page 151.

Tin forms two oxides, the monoxide, $Sn\ O$, and the dioxide, $Sn\ O_2$, these correspond to the oxides of carbon, CO and CO_2; the former of these oxides is almost altogether basic in its character, while the latter most frequently acts as the anhydride of an acid.

Stannous oxide can best be prepared by heating the corresponding hydroxide without access of air. It is a dark brown substance which dissolves in acids to form stannous salts, or in alkalis to form stannites; this latter reaction has already been fully described under stannous chloride. The stannous salts are colorless when formed from a colorless acid, and are readily oxidized when in contact with the air; those insoluble in water, are nearly all soluble in dilute hydrochloric acid.

When tin is heated to a sufficiently high temperature in air or in oxygen, it burns to form the dioxide $Sn\ O_2$, this substance when cold, is a white powder but when hot assumes a yellowish color; after being exposed to a high temperature for some time it becomes insoluble, both in acids and alkalies. The crystallized variety of the oxide, found as the mineral tinstone, is also insoluble; the only means by which this substance can be brought into solution is by fusion with potassium or sodium hydroxide when the respective stannates, $M_2\ Sn\ O_3$, of the metals are formed.

Two stannic acids, identical in gravimetric composition but differing in physical and chemical properties, are derived from the anhydride $Sn\ O_2$; both have the formula $H_2\ Sn\ O_3$. Ordinary stannic acid can be formed by adding exactly enough potassium hydroxide solution to a solution of stannic chloride to precipitate stannic hydroxide:

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* Stannous chloride also forms double halides with the chlorides of the alkali metals, the double halides of potassium are $K\ Sn\ Cl_3 + H_2 O$ and $K_2\ Sn\ Cl_4 + 2\ H_2 O$.

$$Sn\ Cl_4 + 4\ K\ O\ H = Sn\ (O\ H)_4 + 4\ K\ Cl;$$

this substance separates as a jelly which resembles silicic acid. When this is dried it loses water and changes to a gum-arabic like mass which has approximately the formula $H_2\ Sn\ O_3$. This variety of stannic acid is readily soluble both in acids and alkalies. The other form of stannic acid, generally called metastannic acid, is presumably a polymeric form of ordinary stannic acid, so that if the molecule of the latter were $H_2\ Sn\ O_3$ that of the former would be expressed by $n\ (H_2\ Sn\ O_3)$. Metastannic acid is produced in the form of an insoluble white powder when tin is oxidized by means of strong and hot nitric acid; when carefully dried in a vacuum it has the formula $H_2\ Sn\ O_3$; it is insoluble in acids and when glowed loses water and changes into the dioxide of tin. If metastannic acid is digested with hydrochloric acid for some time, the hydrochloric acid then poured off and pure water added, the stannic chloride so formed will dissolve; on addition of alkalis to this solution, however, metastannic acid is once more precipitated. When metastannic acid is boiled with sodium hydroxide it is converted into the metastannate of sodium, which can be dissolved by pouring off the excess of caustic soda solution and then adding pure water. Fusion with solid caustic alkalis converts metastannic acid into salts of ordinary stannic acid.

Stannic chloride, or what amounts to the same thing, the solution of either stannic acid or metastannic acid in hydrochloric acid, resembles the chlorides of the not metals in so far as it is converted into the corresponding acid by boiling with water, this decomposition is, however, only partial, for if a solution of ordinary stannic acid in hydrochloric acid is boiled in a retort, the volatile stannic chloride passes over unchanged in company with the water and hydrochloric acid, while very little stannic acid will remain behind; on the other hand, a solution of stannic chloride derived from metastannic acid is completely decomposed into that acid by boiling, while no stannic chloride whatever will pass over. Only the stannates of the alkali metals are soluble in water, in that way these salts resemble those of silicic and carbonic acids.

Tin forms two sulphides, $Sn\ S$ and $Sn\ S_2$, in formula these correspond to the oxides. The monosulphide, $Sn\ S$, can be produced by adding hydrogen sulphide to an acidulated solution of a stannous salt. The sulphide is a brownish black powder which is insoluble in dilute acids but is dissolved by concentrated hydrochloric acid or by aqua regia, in the latter case stannic chloride is formed. Simple sulphides of the alkalis scarcely attack it; it is dissolved by the polysulphides (see page 151, foot note) because the latter sulphurize it to form salts of sulphostannic acid in a manner exactly similar to their action on the trisulphide of antimony (see page 246). The disulphide of tin, $Sn\ S_2$, can be precipitated from a weakly acid solution of stannic chloride by means of hydrogen sulphide, it forms a yellow precipitate which is not dissolved by dilute acids but which is soluble in strong hydrochloric acid or aqua regia, with the latter reagent it forms stannic chloride. It is readily attacked by either the hydroxides or sulphides of the alkalis (see page 235 and foot note) for in the former case a mixture of stannate and sulphostannate is formed* while in the latter the sulphostannate alone is produced.† This behavior of tin is very much like that of antimony or arsenic under similar circumstances (see pages 235 and 245). On addition of acids to the solution of sulphostannates, stannic sulphide is precipitated, $Sn\ S_3\ K_2 + 2\ H\ Cl = 2\ K\ Cl + H_2\ S + Sn\ S_2$, for the sulphostannic acid which would be formed at once breaks down into hydrogen sulphide and the disulphide of tin; it will be noticed that the formulæ of the sulphostannates correspond to those of the salts of trithio carbonic acid (see page 281).

The compounds of tin show an almost perfect concordance with those of carbon and silicon when the formulæ alone are considered; chemically, however, the acid nature of the substances in question is materially reduced because of the metallic character belonging to tin; this metallic character becomes much more pronounced in the next element of the family, namely lead, so that the oxides of that element are for the most part basic.

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*$3\ Sn\ S_2 + 6\ KOH = Sn\ O_3\ K_2 + 2 Sn\ S_3\ K_2 + 3\ H_2\ O$.

†$Sn\ S_2 + K_2\ S = Sn\ S_3\ K_2$.

The relationship between the compounds discussed in this chapter will be seen from the following table:

TIN AND CARBON.

OXIDES.		CHLORIDES.		ACIDS.		SULPHIDES		
CO	SnO	——	$SnCl_2$	——	$H_2Sn_2O_3$	——	SnS	Forms no sulpho salts.
CO_2	SnO_2	CCl_4	$SnCl_4$	H_2CO_3	H_2SnO_3	CS_2	SnS_2	Forms sulpho salts M_2XS_3.

The oxide SnO is both basic and acidic.
It dissolves in acids as follows:—$SnO + 2HX = SnX_2 + H_2O$.
" " " bases " " :—$2SnO + 2MOH = Sn_2O_3M_2 + H_2O$.
The oxide SnO_2 is both basic and acidic.
It dissolves in halhydric acids as follows:—$SnO_2 + 4HX = SnX_4 + 2H_2O$.
" " " bases " " :—$SnO_2 + 2MOH = SnO_3M_2 + H_2O$.

ORDINARY STANNIC ACID H_2SnO_3.	METASTANNIC ACID, H_2SnO_3.
Derived from an oxide soluble in acids and alkalis.	Derived from an oxide insoluble in acids and alkalis.
The chloride, $SnCl_4$, derived from it is volatile in the vapors of dilute hydrochloric acid.	The chloride, $SnCl_4$, derived from it is not volatile with water vapors (metastannic chloride, it decomposes into hydrochloric acid and metastannic acid when the solution is boiled.
Sodium hydroxide readily dissolves it in the cold forming ordinary stannate of sodium.	Sodium hydroxide, when boiling, forms metastannate of sodium, which is soluble in water.
Ordinary stannic chloride on addition of alkalis precipitates ordinary stannic acid.	Metastannic chloride on addition of alkalis precipitates metastannic acid.

CHAPTER XLV.

LEAD AND ITS COMPOUNDS.

Lead: Symbol, Pb; atomic weight, 206.95.

The element is seldom found uncombined as a mineral. Its most important natural compound is the sulphide $Pb\ S$, which occurs widely distributed as galena or galenite. The carbonate, cerussite, $Pb\ C\ O_3$, the sulphate, anglesite, $Pb\ S\ O_4$, the chromate, phosphate and molybdate are also not infrequently met with.

Lead is one of the metals which has been known since the oldest times, having been familiar to the Israelites. The Romans made much the same use of the metal as we do at the present time, for they constructed water pipes of it and prepared a solder composed of two parts of lead and one of tin.

The lead which is met with as a commercial product usually contains copper, iron and traces of silver. It is prepared by heating the sulphide with finely divided iron:

$$Pb\ S + Fe = Fe\ S + Pb,$$

this operation being conducted in tall furnaces, which, in shape, resemble the blast furnaces for the manufacture of pig iron. Another method for the production of the metal consists in roasting the sulphide in a current of air, by which means it is in part oxidized, so that a mixture of the sulphate, oxide and sulphide are formed, and when this mixture is heated to a higher temperature the sulphate and oxide are finally reduced by the sulphide which is still present; the sulphur passes off in the form of sulphur dioxide, while the lead remains behind. The crude lead contains silver, antimony, arsenic, copper, iron and zinc; the oxidizable impurities are removed by melting the metal in the air. When silver is present in sufficient quantity to pay for its isolation, the entire mass is melted and subjected to a blast of air, by which means lead oxide is produced, the latter melts and is run off from the surface, while the silver remains behind unchanged. The lead oxide so formed can then be once more reduced to lead by means of charcoal. Another method for removing the silver consists in melting the silver-bearing lead and then allowing the mass to cool slowly; pure lead crystallizes at first, this can be removed by means of a ladle, while the molten mass remaining, which is very rich in silver, can be treated according to the method mentioned above; or the silver can be removed by melting the lead with zinc, for zinc only mixes with lead in a small proportion, but is able to disolve all of the silver.

Lead is a metal having a bluish gray color and metallic lustre, it is malleable and easily fused, its melting point is 330°, and it can be boiled at a high white heat. The metal crystallizes in octahedra, its specific gravity is 11.4; when freshly cut the bright metallic surface soon becomes covered with a layer of the oxide which, however, protects the remainder from further corrosion. If a piece of zinc is placed in a solution of a lead salt, the lead will separate in a crystalline form, while the zinc takes its place:

$$Zn + Pb\ (NO_3)_2 = Zn\ (NO_3)_2 + Pb;$$

similar substitutions are not infrequently met with in the chemistry of other metals (see page 302 and foot note).

When lead is covered with water which is in contact with the air, it becomes covered with a layer of lead hydroxide, the latter substance is to a certain extent soluble in water; as a consequence water which has passed through new lead pipes contains more or less of the hydroxide in solution and may, for this reason, prove to be highly poisonous; however, hard water gradually changes the hydroxide into the entirely insoluble carbonate, so that, in time, the pipes become covered with a protective coating. In dealing with lead pipes, however, care must be taken to have no decaying organic substances present, for such impurities may remove the carbonate and greatly increase the solubility of the lead.

Lead is not readily attacked by hydrochloric or cold sulphuric acid; hot and concentrated sulphuric acid has some effect on it, as is evinced by the fact that commercial sulphuric acid always contains lead; nitric acid readily dissolves the metal to form lead nitrate.

Lead quite readily enters into a number of alloys, some of which have already been mentioned (see page 241), while the metal is easily amalgamated by mercury.

Lead forms four oxides, Pb_2O, suboxide of lead, $Pb O$, lead monoxide, $Pb_2 O_3$, lead trioxide, and $Pb O_2$ lead dioxide or lead hyperoxide. Of these the oxides $Pb O$ and $Pb O_2$ are the most important; the monoxide, $Pb O$, corresponds to carbon monoxide and the dioxide, $Pb O_2$, to carbon dioxide.

The oxide of lead, $Pb O$, can easily be produced by heating the nitrate (see page 193), or, like other oxides of weakly pronounced metals, it can be formed by heating the hydroxide:

$$Pb (OH)_2 = Pb O + H_2 O.$$

This oxide of lead is a yellow powder which is easily melted to an orange-colored mass (litharge). The hydroxide of lead separates as a white precipitate when a base is added to a solution of a lead salt:

$$Pb (N O_3)_2 + 2 Na O H = Pb (O H)_2 + 2 Na N O_3,$$

and, like stannous hydroxide, it is both a base and an acid. As a result of its basic proper ties,it readily dissolves in acids to form salts:

$$Pb (O H)_2 + 2 H N O_3 = Pb (N O_3)_2 + 2 H_2 O;$$

and because of its acid properties it dissolves in pronounced alkalis:

$$Pb (O H)_2 + 2 K O H = Pb (O K)_2 + 2 H_2 O$$

(compare with stannous hydroxide, page 304). The salts of lead can be formed by dissolving either the oxide or hydroxide in acids, and, being salts of a pronounced metal, they are more or less stable; they are poisonous when in a soluble form. Among the most important salts of lead are the chloride, $Pb Cl_2$, sulphate, $Pb S O_4$, and chromate, $Pb Cr O_4$, which are insoluble or nearly insoluble in water; they can therefore be produced from the soluble lead salts by the addition of a soluble chloride sulphate or carbonate. The soluble carbonates of the alkalis cause a precipitate of basic carbonate of lead, $Pb (OH)_2 Pb C O_3$; this substance is white lead. Among the important soluble lead salts, the acetate ($Pb (C_2 H_3 O_2)_2$, sugar of lead) may be mentioned. One interesting fact as regards lead salts is the isomorphism which the sulphate displays with the sulphates of the very pronouncedly metallic alkaline earths, calcium, barium and strontium, and the isomorphism of the carbonate with carbonates forming the arragonite group (page 281).* This relationship shows us that the pronounced metallic properties of lead have caused it to depart so far from the family type that its salts resemble those of the most characteristic divalent metals; this isomorphism is also displayed in the case of some other lead compounds.

The oxide of lead next in importance to the monoxide, $Pb\,O$, is the dioxide or hyperoxide, $Pb\,O_2$, this substance has only very weak basic or acid properties. It belongs to the class of hyperoxides of which manganese dioxide is, perhaps, the best known representative; the hyperoxides are all neutral or nearly neutral bodies which, when heated with sulphuric acid, give off oxygen and change to the sulphate of the oxide MO, and which, when treated with hydrochloric acid, liberate chlorine. The dioxide of lead is occasionally found in nature, it can be formed in the laboratory by treating the oxide $Pb_3\,O_4$ † with nitric acid or by oxidizing the acetate of lead with a solution of chloride of lime.

Lead dioxide is a dark brown powder which is a powerful oxidizing agent, indeed, it can oxidize sulphur dioxide so readily that the heat of the reaction may even cause it to glow, provided it is finely divided and placed in an atmosphere of the gas. When in contact with strong bases it dissolves to form salts of an acid, plumbic acid, $H_2\,Pb\,O_3$, which, in formula, corresponds to carbonic acid but which, like the latter, does not exist in the free state; only a very few salts of this acid are known. On the other hand the dioxide is soluble in some acids, although the salts which are presumably formed by this action have not been isolated. The suboxide of lead, $Pb_2\,O$ and the sesquioxide, $Pb_2\,O_3$ are of little importance. The metallic character of lead is so predominent that the nature of its oxides is very much at variance with that of the oxides of the elements at the beginning of this family, indeed, in the formation and character of the compounds

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* The carbonates of calcium, barium, manganese and iron.

† The red oxide of lead $Pb_3\,O_4$ can be looked upon as a mixture of the oxides $Pb\,O$ and $Pb\,O_2$:

$$2\,Pb\,O + Pb\,O_2 = Pb_3\,O_4;$$

the nitric acid dissolves out the monoxide $Pb\,O$ and leaves the dioxide $Pb\,O_2$; compare this formula with $Mn_3\,O_4$ and $Fe_3\,O_4$.

Pb_3O_4 and PbO_2 lead very much resembles manganese, while the isomorphism of its salts with those of calcium, barium and strontium brings it in close connection with the alkaline earths, on the other hand it is like carbon, silicon and tin, for its oxide PbO_2 shows weakly acid properties. In fact, the chemical characteristics of lead are not very marked in any direction, nor, indeed, is this neutral behavior unexpected, for we find it to be quite a general fact that the elements with high atomic weights and specific gravities display no very pronounced chemical properties, the crowding of a large mass into a small space, as is the case with these elements, is therefore unfavorable for the manifestation of striking chemical phenomena.

Lead forms only one sulphide which has been accurately studied, the monosulphide PbS. This substance is found as the mineral galena, crystallized in cubes of metallic appearance. In the laboratory it can be produced either by direct combination of the elements or by precipitation from acid solutions of lead salts by means of hydrogen sulphide; when so prepared it is a black, amorphous powder which is not attacked by cold hydrochloric acid, but which is attacked by that substance when it is hot and concentrated. Oxidizing agents, such as nitric acid, change it into the insoluble sulphate of lead and a similar transformation is brought about by roasting in the air.

In the following table the most important compounds which have representatives in the chemistry of a number of elements of this family are placed side by side; those acids which are not known in a free state, but salts of which exist, are placed in parentheses:

OXIDES.

CO,	—,	GeO,	SnO,	PbO,
CO_2,	SiO_2,	GeO_2,	SnO_2.	PbO_2.

CHLORIDES.

—,	—,	$GeCl_2$,	$SnCl_2$.	$PbCl_2$.
CCl_4,	$SiCl_4$,	$GeCl_4$,	$SnCl_4$,	$PbCl_4$.*

ACIDS.

—,	—,	—,	$H_2Sn_2O_3$,	$Pb(OH)_2$.
(H_2CO_3),	H_2SiO_3.	—,	H_2SnO_3,	(H_2PbO_3).

SALTS.

M_2CO_3,	M_2SiO_3,	—,	M_2SnO_3,	M_2PbO_3.

SULPHIDES.

—,	—,	—,	SnS,	PbS,
CS_2,	SiS_2,	GeS_2,	SnS_2,	—.

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* Presumably formed because the dioxide dissolves in acids.

CHAPTER XLVI.

THE ELEMENTS OF THE BORON FAMILY. (THE EARTHS).

The elements of the family of which boron is the member with the smallest atomic weight, are the last which will be considered where any purely not-metallic element occurs. As has been repeatedly mentioned, the groups of elements become, as a whole, more metallic in their nature as the atomic weights diminish, this fact is readily recognized by comparing the various families in the order in which they have been studied, as is shown in the table on page 255. In the nitrogen group there are four elements, nitrogen, phosphorus, arsenic and antimony which could be classed with the not-metals, in that of carbon there are but two, carbon and silicon, while in the one under consideration, boron alone appears to us with pronouncedly not-metallic characteristics, while even this element is unable to form a gaseous hydrogen compound of sufficient stability to render an accurate study of its properties practicable.

The elements comprising the boron family are:

Boron,	atomic	weight.	11;	Carbon,	atomic	weight,	12;[*]
Aluminium,	"	"	27;	Silicon,	"	"	28.4;
Gallium,	"	"	69;	Germanium,	"	"	72.3;
Indium,	"	"	113.7:	Tin,	"	"	119.;
Thallium,	"	"	204.18;	Lead,	"	"	206.95.

The highest valence toward oxygen displayed by the elements of the nitrogen family is five, as is shown by the existence of the pentoxides, $X_2\,O_5$; in the carbon family the power of uniting with oxygen is exhausted when the dioxide, XO_2, in which the element is quadrivalent, is reached, while in the boron group, with a return to the type of oxide shown by nitrogen and its fellows, the highest valence displayed toward oxygen is only three, so that the characteristic oxides of this group have the formula $X_2\,O_3$. These oxides, of course, suffer a diminution in their acidic character the greater the atomic weight of the element forming them is, so that boron trioxide, $B_2 O_3$, acts as an acidic anhydride under all circumstances, aluminium trioxide, $Al_2 O_3$, is both basic and acidic, the oxide of gallium, $Ga_2 O_3$, displays the same character, while the oxide of indium, $In_2 O_3$, is almost exclusively basic, for it dissolves in caustic alkalis only with difficulty and the unstable compound so formed is broken up by warming the solution; finally, the trioxide of thallium, $Tl_2 O_3$, is not affected by the reagents in question; from the above comparative statement it follows that the oxides $X_2 O_3$ are more *basic* the greater the atomic weight of X. As the elements in the family increase in atomic weight, they display the same tendency to form a number of oxides which is observed in the case of lead in the carbon family, this fact will become apparent by a study of the following table:

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[*] For the purpose of comparing atomic weights the elements of the carbon family have been placed in a parallel column.

Boron forms one oxide, $B_2 O_3$;
Aluminium forms one oxide, $Al_2 O_3$;
Gallium " two oxides, Ga O, and $Ga_2 O_3$;
Indium " " " In O and $In_2 O_3$;
Thallium " three " Tl_2 O, $Tl_2 O_3$, and $Tl O_2$.

The oxides with least amount of oxygen which are derived from any given element, are, without exception, basic in their character while the trioxides, with the exception of that of thallium, are both basic and acidic. The majority of the salts which contain an element which is a member of this family are derived from the trioxide $X_2 O_3$.

What is true of the oxides is also true of the halogene compounds, the elements with high atomic weights each are capable of forming more than one chloride, bromide or iodide, while aluminium and boron are confined to one apiece. The trihalide, like the trioxide, is the compound common to all of the members of the family. The relationship between these compounds can be seen by examining the following table, as will be noticed, the rule which held good in all the preceeding families, namely, that the boiling points of the trichlorides are higher the greater the molecular weight of the compound, is also without exception in this group.

$B Cl_3$, liquid, boils at 17°;
$Al Cl_3$, solid, melts at 180°, boils at 183°;
$Ga Cl_3$, solid, melts at 75.5°, boils at 220°;
$In Cl_3$, solid, volatilizes at red heat without melting;
$Tl Cl_3$, gives off chlorine when heated and changes to the chloride Tl Cl.

In addition to the chlorides given above, gallium forms a compound with the formula $Ga Cl_2$, indium the chlorides In Cl and $In Cl_2$, while thallium also has a monochloride, Tl Cl.

CHAPTER XLVII.

BORON AND ITS COMPOUNDS.

Boron: Symbol, B; atomic weight, 11.

In its physical characteristics boron bears a marked resemblance to carbon, the element having the next highest atomic weight to its own, but in the chemistry of its oxides and chlorides, boron is very much like the members of the nitrogen family.

Boron is never found uncombined in mineral deposits. Its compounds, which not infrequently occur in nature, are either salts of boric acid or the acid itself. The most important of these minerals are:

Borax (tinkal) $Na\,H\,(B\,O_2)_2,\,4\,H_2\,O$;
Borocalcite. $Ca\,H_2\,(B\,O_2)_4,\,5\,H_2\,O$.

The borates of other metals, for instance of iron and magnesium, are also found, while solutions of boric acid sometimes occur in lagoons of volcanic regions.

Although the element was not isolated until 1807 * and was not accurately described until 1824,† its compounds, especially tinkal, occurring as they do in mineral deposits, were known in very early times, the natural borax having become familiar to Europeans by importations from India.

Boron can be isolated by heating sodium with the oxide $B_2\,O_3$ or potassium with potassium fluoborate, $K\,B\,F_4$. When so obtained it is an amorphous brownish black powder which greatly resembles silicon in appearance; it is quite readily dissolved by melted aluminium and, when the metal containing the boron is cooled, the latter separates in the form of reddish-yellow, diamond-like crystals which are very hard and lustrous. When the aluminium has only been heated to a temperature just above its melting point, then the dissolved boron appears in a graphitoidal form. Elementary boron, therefore, displays modifications similar to those peculiar to carbon. The specific gravity of boron is 2.68; it is infusible.

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* By Guy Lussac and Thénard.

† By Berzelius.

When heated in the air, amorphous boron burns to form the trioxide $B_2 O_3$; the same modification of the element is readily oxidized by nitric acid or even by concentrated sulphuric acid,* boric acid, $B O_3 H_3$, being produced. Boron can unite directly with chlorine, bromine, with some metals, and with nitrogen.

A gaseous hydrogen compound of boron was not known until quite recently.† It was then prepared in an impure state by treating the boride of magnesium with hydrochloric acid; this method corresponds to the one by which silicon hydride, $Si H_4$, and pure arsine and stibine are produced. Hydrogen boride is very unstable; it burns in air or in oxygen with a bright green flame and it is slightly soluble in water. The formula assigned to the gas is $B H_3$, but a more extended investigation of its composition is necessary.

The halogene compounds of boron correspond to the general formula of $B X_3$, so that in structure they are identical with the trihalides of the nitrogen family. The trichloride and trifloride are the only representatives of these compounds which we need consider. The trichloride is formed by the direct union of chlorine and boron;‡ when first discovered it was supposed to be a gas at ordinary temperatures, but subsequent investigations proved it to be a liquid with a boiling point at 17°. Being the chloride of a not-metal, boron trichloride is, of course, readily decomposed by water, and *normal* or *ortho* boric acid results from this decomposition:

$$B \left\{ \begin{matrix} Cl + HOH \\ Cl + HOH \\ Cl + HOH \end{matrix} \right. = B \left\{ \begin{matrix} OH \\ OH \\ OH \end{matrix} \right. + 3\, H\, Cl.$$

It will be noticed that this change is parallel to the one undergone by phosphorus trichloride when in the presence of water, (see pages 77 and 212).

Boron trifluoride is a colorless gas and is interesting because its chemical properties are much like those of the tetrafluoride of silicon (see page 290). It can be prepared by treating the dry trioxide of boron with hydrofluoric acid * so that, in this reaction *boron trioxide is a base.*

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* Compare the action of amorphous carbon (charcoal) on nitric acid, note 59 of appendix, and on sulphuric acid, page 132.

† In 1881, by Jones and Taylor.

‡ By passing chlorine over an intimate mixture of boron and carbon heated to redness. This method of preparation is exactly like the one employed in the formation of the chloride of silicon, $Si\, Cl_4$.

$$B_2 O_3 + 6 HF = 2 BF_3 + 3 H_2 O.†$$

Boron trifluoride, when passed into water undergoes a decomposition similar to that experienced by silicon tetrafluoride, for it breaks down into boric and fluoboric acids, (see page 291).

$$4 BF_3 + 3 H_2 O = 3 H BF_4 + B (OH)_3.$$

Fluoboric acid bears a very close resemblance to fluosilicic acid. It forms fluoborates with the general formula of MBF_4 when it is brought in contact with the hydroxides of the alkali metals and in these compounds fluorine must necessarily be considered as a bivalent element for reasons identical with those brought forward in the discussion of silicofluorides on page 291.

The only oxide of boron is the trioxide, $B_2 O_3$. The latter can be formed either by burning amorphous boron or, as is more expedient, by heating the hydroxide $B (OH)_3$ (boric acid) to redness; the trioxide forms a glass-like mass which is soluble in water and which, as it volatilizes only at a very high temperature, will, when heated with the salts of other, volatile acids, finally decompose those salts and form borates. For the same reason, fused boric acid is able to dissolve the great majority of metallic oxides.[75]

Boric acid, $(B (OH)_3$, not infrequently occurs in natural deposits, it being found in a crystalline state in the neighborhood of the fumaroles‡ of Tuscany, the acid so found is called "sassolin." The water of the lagoons in this region contains about one-tenth per cent. of boric acid, this amount is increased to as much as one per cent. by collecting the water in cisterns and then allowing the vapors, charged with boric acid, to condense in these receptacles; the cistern water is finally evaporated in flat leaden pans which are warmed by the steam which is escaping from the earth; the solid residue which remains, containing about 75 per cent. of boric acid, is purified by recrystallization. Boric acid is also prepared for commercial use by decomposing natural borax* or borocalcite by means of acids.

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* By mixing the trioxide, $B_2 O_3$, with fluorspar, fusing and then adding sulphuric acid to the mass when cool.

† Note the resemblance of this reaction to the one employed in preparing the fluoride of silicon.

‡ Fumaroles are jets of water vapor which escape from fissures in the earth in volcanic regions; these vapors condense on the surface and form small lagoons which are kept boiling by the continued injection of hot vapors.

Boric acid is a white, crystalline, flaky solid which, to the touch, has a peculiar fatty feeling; it is tolerably soluble in water, one part of the acid being taken up by twenty-six parts of the solvent at ordinary temperatures. Boron trioxide is also quite soluble in alcohol; when this solution is lighted, the solvent burns with a characteristic green flame.[76]

The usual form of boric acid is orthoboric acid, when this substance is heated to 100°, water is given off and metaboric acid is produced:

$$B \begin{cases} OH \\ OH \\ OH \end{cases} = B \begin{cases} O \\ OH \end{cases} + H_2\,O$$

$$B\,(OH)_3 = BO_2\,H + H_2\,O.\dagger$$

When metaboric acid is heated to 100° it is changed to tetraboric acid, which has the formula $H_2\,B_4\,O_7$, its structure being similar to those of di and trisilicic acids (see page 296). The most common salt of boric acid, commercial borax, is derived from tetraboric acid. Finally, when tetraboric acid is fused, all of the hydroxyle groups are separated in the form of water, and the anhydride $B_2\,O_3$ is formed.

The metaborates, $M\,B\,O_2$, and the tetraborates, $M_2\,B_4\,O_7$, are the most stable salts of boric acid. The orthoborates, $M_3\,B\,O_3$, are easily decomposed; the organic derivatives of orthoboric acid are, however, quite frequently tolerably stable substances.

The not-metallic properties of the elements of the boron family are not very pronounced, indeed, the element with next higher atomic weight, namely aluminium, is almost invariably metallic in its nature; so that, as a consequence, we would expect boron trioxide to act as a base under some circumstances, and this is found to be the case when we consider that the oxide dissolves in hydrofluoric acid to form boron trifluoride, $B\,F_3$, and is also made apparent by the existence of a phosphate of boron, $B\,P\,O_4$.

Only one oxy, or acid chloride of boron, having a character similar to the chlorides of sulphur and phosporus (see pages 182 and 213) exists. This substance has the formula B O Cl; it is derived from metaboric acid by replacing the hydroxyle group with chlorine; it is decomposed by water.

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*Found in large quantities in some alkaline lakes, for instance in Borax lake, California.

†Compare with the table on page 207.

The sulphide of boron in formula corresponds to the oxide, it can be formed by direct union of the elements. No sulpho-salts derived from this compound are known, indeed it is decomposed with the greatest violence when brought in contact with water, so that in the latter respect it resembles the sulphide of silicon.

Boron is one of the few elements that is capable of direct union with nitrogen. The nitride of boron, B N,* is a white solid, formed by heating an intimate mixture of borax and ammonium chloride. Like cyanogen, it is a stable substance; it is not attacked either by acids or alkalies, but when heated in a current of steam it breaks down into boric acid and ammonia:

$$B\,N + 3\,H_2\,O = B\,(O\,H)_3 + N\,H_3.$$

The occurrence of boric acid in the fumaroles of Tuscany is attributed to the subterranean decomposition of the nitride of boron by means of water vapor.

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* This nitride is therefore analogous to cyanogen, $(C\,N)_2$.

CHAPTER XLVIII.

ALUMINIUM AND ITS COMPOUNDS.

Aluminium: Symbol, Al; atomic weight, 27; specific gravity, 2.5.

Aluminium never occurs as the uncombined metal. Its oxide, hydroxides, fluoride and silicates are, however, very widely distributed in mineral deposits. The chief aluminium compounds which are found in the form of mineral individuals are:

Corundum: $Al_2 O_3$, named ruby when found in red, transparent crystals.
Diaspor: $Al O_2 H$; this hydroxide, in formula, corresponds to metaboric acid.
Beauxite: $Al_2 O (O H)_4$.
Hydrargyllite: $Al (O H)_3$; this substance is the normal aluminium hydroxide.
Cryolite: $3 Na F, Al F_3$.
Spinell: $Mg Al_2 O_4$; a magnesium salt of the hydroxide $Al O_2 H$.

In addition to these oxides and hydroxides and the salts derived from them. aluminium forms a large number of silicates. Among the orthosilicates which contain aluminium are:

Garnet: $Ca_3 Al_2 (Si O_4)_3$.
Muscovite: $K H_2 Al_3 (Si O_4)_3$; and allied to muscovite are the various micas
Kaolin (clay): $H_4 Al_2 Si_2 O_9$.

Some of the most important meta-silicates, for example, hornblende and augite, have already been mentioned, as have also the very important polysilicates which belong to the feldspar group (see page 296).

So extended is the distribution of aluminium in the mineral kingdom that it can safely be asserted that the element is a constituent of the greater number of natural silicates. Basic sulphates and phosphates of aluminium are also not infrequently met with.

Although its compounds are so widely distributed, aluminium itself was not discovered until 1827, when Wöhler prepared the metal by heating powdered aluminium chloride with potassium. At a later date St. Claire Deville introduced the use of sodium, which is comparatively cheap, in place of the very dear metal potassium, and at a still later date Rose improved the process by using cryolite, $Al F_3$, $3 K F$, instead of aluminium chloride. Until very recently, however, all of the aluminium of commerce was prepared by heating the chloride of that metal with sodium, by which reaction sodium chloride and aluminium are formed:

$$Al\,Cl_3 + 3\,Na = Al + 3\,Na\,Cl.$$

In the last four years this expensive process has given way to one which depends on the electric decomposition of fused beauxite by means of a very powerful current, generated by dynamo machines of unusual size. Crushed beauxite is placed in flat iron tanks, which latter constitute one of the electrodes, while a series of extra large pieces of gas carbon, connected by a copper strap, and placed in contact with the crushed mineral, form the other. When the current is turned on, the resistance of the solid beauxite is sufficient to heat the entire mass to its fusing point, and when this stage is reached, cryolite, which by reason of its low melting point and specific gravity will form a protective covering to the beauxite, is added; the electric decomposition of the mass then goes on, aluminium separating in nodular masses. By reason of this improvement in the manufacture of the metal, the price of aluminium has fallen very greatly of late years.

The specific gravity of aluminium is 2.5,* its melting point is 700°; the metal cannot be volatilized. Aluminium is a good conductor of heat; it conducts electricity almost eight times as well as iron does. When covered with concentrated nitric acid the metal is transferred into a condition in which it is not further attacked by the acid; when the metal is in this state it will generate an electric current when placed in contact with ordinary aluminium. A metal acting in this way is said to be in the "passive state." No adequate explanation of this phenomenon has as yet been given.

Aluminium, because of its small specific gravity, its toughness and the difficulty with which it is attacked by the corroding agents which ordinarily come in contact with a metal in general use, will, in the future, have its commercial usefulness limited only by the cost of its production, and, as we have seen, the latter is constantly diminishing. A number of aluminium alloys are finding extended application; perhaps the most important of these is aluminium bronze composed of about ten parts of aluminium to ninety parts of copper; this composition is more easily worked than ordinary bronze, is tougher, is tarnished with difficulty and has the color of gold.

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*This specific gravity is for cast aluminium; hammered aluminium has a specific gravity of 2.67.

Aluminium forms but one series of compounds with the halogenes, these compounds have the general formula $Al\,X_3$ and of these the chloride $Al\,Cl_3$ is the most important. Aluminium chloride is produced by heating powdered aluminium in a current of dry chlorine. Although a solution of aluminium oxide or hydroxide in hydrochloric acid undoubtedly contains aluminium chloride, just as is the case in a similar solution of arsenic trioxide (see page 175), nevertheless, the salt cannot be isolated by evaporating the liquid because, as the trichloride is the halogene compound of a metal with very weakly pronounced metallic properties, it at once breaks down into the hydroxide of aluminium and hydrochloric acid:

$$Al\left\{\begin{array}{l}Cl + HOH\\ Cl + HOH\\ Cl + HOH\end{array}\right. = Al\left\{\begin{array}{l}OH\\ OH\\ OH\end{array}\right. + 3\,H\,Cl.$$

Aluminium chloride is a white, crystalline solid which fumes when in contact with the air; it greedily absorbs moisture and, while giving off hydrochloric acid, changes into aluminium hydroxide; it boils at 180°. The vapor density of aluminium chloride was formerly supposed to be 9.34, if air is taken as unity, this specific gravity corresponds to a molecular weight of 267; and a formula $Al_2\,Cl_6$. This experimental evidence inaugurated a theory of the quadrivalence of aluminium in its trichloride, for the structure of the latter compound, were the molecule to have the formula $Al_2\,Cl_6$ would be as follows:

$$\left.\begin{array}{r}Cl\\ Cl\\ Cl\end{array}\right\}Al - Al\left\{\begin{array}{l}Cl\\ Cl\\ Cl.\end{array}\right.$$

A similar constitution was assigned to the trichloride of iron, which substance likewise was supposed to have a molecule corresponding to the formula $Fe_2\,Cl_6$. The latest investigations of Nilssen and Petterson* have shown, however, that the vapor density of 9.34 found for aluminium chloride is only incidental to a certain temperature † and this specific gravity steadily diminishes as the heat is increased, until it reaches 4.6 at 800°; this latter number remains constant up to 1500°, from this it is evident that the molecular weight of aluminium chloride is 133.5; the formula of this compound is consequently $Al\ Cl_3$,* so that aluminium must be regarded as a trivalent element. Even if no vapor density determinations of the chloride of iron had been made, it would seem probable that the trichloride has the formula of $Fe\ Cl_3$, for iron can replace aluminium in isomorphous mixtures, so that a difference in the valence of the two elements in compounds derived from the trioxide $M_2\ O_3$ seems scarcely probable.

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* Zeitschrift für Physikalische Chemie, IV, 206.

† 357°.

The halogene compounds of aluminium possess the power in a marked degree of forming double salts with the halides of other metals. Formerly these double salts were looked upon as molecular additions, formed of a finished molecule of some halogene salts of aluminium uniting with the halide of an alkali metal. Such a theory really means that we have no knowledge of the structure of such compounds, although in maintaining it we must believe that the molecules have a residuum of chemism at their disposal. The theory of simple molecular addition would no longer be tenable if any of the double salts could be obtained as gases with unchanged composition, and in the case of the double chloride of sodium and aluminium, Deville states that the compound can be vaporized without separating it into molecules of $Al\ Cl_3$ and $Na\ Cl$. A theory which is of late being regarded with considerable favor is the one which supposes that, in the double halides, the halogene compounds of such weakly metallic elements as arsenic, antimony, bismuth, or aluminium assume the role of acidic anhydrides, while the halides of the alkali metals are the bases, and in order to maintain such a theory the assumption is inevitable that the atoms of the halogenes can, under certain circumstances, become divalent; such a belief is strengthened by the existence of acids like fluosilicic acid, $H_2\ Si\ F_6$, and fluoboric acid, $H\ B\ F_4$ (see pages 291, 318). That structures similar to those of the salts of oxy-acids are possesed by the double halide salts seems more than probable if we consider the following: "When a halide of any element combines with the halide of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater, and is generally less than the number of halogene atoms contained in the latter."[*] It must be confessed, however, that the rule has a number of exceptions. The chlorides of aluminium and potassium and of aluminium and sodium have the formulæ $\mathrm{Al\,Cl_3,\ K\,Cl}$ and $\mathrm{Al\,Cl_3,\ Na\,Cl}$, and if we regard $\mathrm{Al\,Cl_3}$ as analogous to an acidic anhydride, and K Cl and Na Cl as analogous to bases, the structure of these compounds would be as follows:

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*This discovery is further borne out by the fact that certain organic derivatives of aluminium which have been obtained as gases undoubtedly contain that element in a trivalent form.

$$\mathrm{Al}\left\{\begin{matrix}\mathrm{Cl_2}\\ \mathrm{Cl_2\,K}\end{matrix}\right. \quad \text{and} \quad \mathrm{Al}\left\{\begin{matrix}\mathrm{Cl_2}\\ \mathrm{Cl_2\,Na};\end{matrix}\right.$$

the parallelism between these formulæ and those of the corresponding oxy-compounds becomes apparent when we consider the structure of the latter, namely:

$$\mathrm{Al}\left\{\begin{matrix}\mathrm{O}\\ \mathrm{O\,K}\end{matrix}\right. \quad \text{and} \quad \mathrm{Al}\left\{\begin{matrix}\mathrm{O}\\ \mathrm{O\,Na}.\end{matrix}\right.$$

The double fluorides of aluminium are of two kinds, the first of which with the general formula $\mathrm{Al}\left\{\begin{matrix}\mathrm{F_2}\\ \mathrm{F_2\,M}\end{matrix}\right.$ are constructed similarly to the chlorine compounds, while second, with the general formula

$$\mathrm{Al}\left\{\begin{matrix}\mathrm{F_2\,M}\\ \mathrm{F_2\,M},\\ \mathrm{F_2\,M}\end{matrix}\right. \text{ correspond to the theoretical ortho-aluminates, } \mathrm{Al}\left\{\begin{matrix}\mathrm{O\,M}^{\dagger}\\ \mathrm{O\,M}\\ \mathrm{O\,M}.\end{matrix}\right.$$

In addition to the substances which have just been discovered, a number of compounds in which aluminium chloride is a base are known; an example would be the compound $\mathrm{Al\,Cl_3,\ P\,Cl_5}$.[‡] The existence of these double chlorides once more reminds us of the great resemblance between the chemistry of the halogenes and that of oxygen (see pages 60, 61 and 152).

Aluminium forms but one oxide, thet rioxide $\mathrm{Al_2\,O_3}$. This substance occurs as the mineral corundum, which, when finely divided and mixed with oxide of iron, is called emery. The transparent, red crystals of the oxide are called ruby. Aluminium trioxide is produced when aluminium is glowed in air or in oxygen, or when the hydroxide is heated; the latter substance, because it is insoluble in water, is precipitated from solutions of aluminium salts by adding ammonia water:

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[*] Remsen, *American Chemical Journal*, 14, 85.

[†] In generalizing in regard to these double halides we must except the double cyanides, page 285.

[‡] Compare the formulæ $\mathrm{Al\,P\,Cl_8}$ and $\mathrm{Al\,P\,O_4}$.

$$Al\,Cl_3 + 3\,N\,H_3 + 3\,H_2\,O = Al\,(OH)_3 + 3\,N\,H_4\,Cl.$$
$$2\,Al\,(OH)_3 = Al_2\,O_3 + 3\,H_2\,O.$$

The oxide which has been heated to redness, or the naturally occurring crystalline varieties, are insoluble both in acids, water or solutions of the alkalis; they can be brought into solution by fusing with caustic alkalis. The oxide which has not been heated is both basic and acidic, for it dissolves in acids to form the salts of aluminium and in bases to form aluminates.

Several hydroxides are derived from aluminium trioxide. The first of these, the normal hydroxide $Al\,(OH)_3$, is precipitated from solutions of aluminium salts by ammonia water or caustic alkalis; in using the latter reagents, however, care must be taken not to add an excess, otherwise solution of the hydroxide and the formation of an aluminate take place. The remaining hydroxides are derived from the normal compound by loss of water; the most important of these is the meta-hydroxide, $Al\,O_2\,H$,* which is found as the mineral diaspor. The salts of this substance, formed by replacing the hydrogen with a metal, are the types of the important group of minerals known as the spinells. The spinells are a group of isomorphous compounds, each one of which is derived from a hydroxide, $X\left\{\begin{matrix}O\\OH,\end{matrix}\right.$ in which hydroxide X can be either trivalent aluminium, iron or chromium; the hydrogen of this hydroxide is replaced by a divalent metal, M'', so that the general formula for these minerals would be $M''\,(X\,O_2)_2$; M'' is either divalent iron, magnesium, manganese or zinc. The typical spinell is the aluminate of magnesium, $Mg\,(Al\,O_2)_2$. When meta-aluminium hydroxide is dissolved in caustic alkalies, the solution, unless it is a very concentrated one containing an excess of the solvent, probably contains the meta-aluminate of the particular alkali metal used;

$$Al\,O_2\,H + M\,O\,H = Al\,O_2\,M + H_2\,O.$$

In addition to the ortho and meta-hydroxides, another hydroxide of aluminium, $Al_2\,O_5\,H_4$, is frequently met with in the mineral beauxite; this substance is formed by the separation of water between two formula weights of ortho-aluminium hydroxide (see page 296).

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* Corresponding in formula to metaboric acid, $B\,O_2\,H$.

The normal hydroxide of aluminium, when freshly precipitated, is a gelatinous substance which readily dissolves in acids to form the salts of aluminium; among these, perhaps, the most important are the sulphates.

ALUMINIUM SULPHATE: $Al_2 (S O_4)_3 + 8 H_2 O$; formed by dissolving aluminium oxide or hydroxide in sulphuric acid and evaporating to dryness. When heated it loses its water of crystallization at 100°, and at red heat gives off sulphur trioxide, leaving aluminium oxide behind: $Al_2 (S O_4)_3 = Al_2 O_3 + 3 S O_3$.

ALUMINIUM AND POTASSIUM SULPHATE: $Al_2 (S O_4)_3, K_2 S O_4 + 24 H_2 O$. This substance is commonly known as alum. The alums are double salts composed of one formula weight of the sulphate of a monovalent alkali metal or of ammonia combined with the sulphate of a trivalent metal, the general formula being $M'''_2 (S O_4)_3, M_2 S O_4 + 24 H_2 O$. M''' can be either aluminium, iron, chromium or one of the rarer metals belonging to the boron family; M can be any one of the alkali metals, or ammonium. The alums are all isomorphous and crystallize in in octahedra belonging to the regular system. They can be formed by evaporating to dryness a mixture of the solutions of the sulphates of any one of the trivalent metals mentioned and of one of the alkalis.

A number of basic sulphates of aluminium are known; some of these are found in the form of mineral deposits. Several neutral and basic phosphates of aluminium occur in nature; perhaps the most important of these is wavellite, $2 Al P O_4, Al (O H)_3 + 9 H_2 O$. When sodium phosphate is added to the neutral solution of an aluminium salt, the tertiary phosphate of aluminium, $Al P O_4$, is produced in the form of an insoluble precipitate; this is changed to a basic phosphate by boiling with ammonia water.

As has been mentioned, aluminium is a constituent of a very large number of silicates, some of which have already been discussed. Of these the most important is undoubtedly the hydrated tertiary orthosilicate which approximately has the composition expressed by the formula $H_2 Al_2 (Si O_4)_2 + H_2 O$ and which is known as clay or kaolin. This substance is the result of the disintegration of feldspar or of rocks which contain a large proportion of that mineral, as some granites do; owing to the destructive action of the weather, the feldspar decomposes into aluminium silicate, silicon dioxide and the silicates of the alkali metals; the latter are washed away, brought into the soil, and there, after interacting with other chemical constituents with which they come in contact, they are in a proper condition to be absorbed by plants. The kaolin which remains on the spot where disintegration occurrs is, owing to the formation of silicon dioxide during the process of destruction, is necessarily mixed with that substance and not infrequently contains mica; some clays, however, are washed to some distance from their place of formation and there may have taken up the most varied impurities, like the carbonates of calcium and magnesium, the oxides of iron and of maganese, quartz sand and other materials.

Clay is generally found in an impure condition, when this is pressed into molds and baked in a kiln, it becomes hard and is known as brick. Pure kaolin is white in color and is used in the manufacture of porcelain, when it is moist it forms a very plastic mass. Kaolin which is entirely free from iron is alone useful in the manufacture of porcelain because, as the mass is heated to the point where it softens and becomes glassy, any foreign substances would make themselves apparent by their color. The clay is purified by being agitated with water, when the coarser portion separates at the bottom, the finer parts are molded into forms, dried, and finally heated to a red heat. This latter treatment makes the article in the process of manufacture strong but leaves it porous, in order to finish the same it is covered with a mixture of silicon dioxide, aluminium oxide and sodium carbonate, which ingredients form an easily fusible glass, and it is then heated to a temperature at which the clay begins to soften and at which the glazing has been converted into a coating of transparent glass. Fayence is made of clay of somewhat coarser structure than that used in the manufacture of porcelain, the thickness of the dishes is greater and the ware is not heated to a temperature high enough to convert it into the glass-like mass which forms porcelain. Fayence is covered with a glaze which is much like that given above, with the difference that some lead oxide is added. Common stone ware is made from clay which is even more impure than that from which fayence is prepared, the glazing is either put on by covering the ware before burning with the mixture to be used, or it is made by throwing common salt on the utensils while they are being heated in the furnace; the salt evaporates, comes in contact with the surface of the materials used and covers it with a fusible soda glass.

But one sulphide of aluminium, with a formula $Al_2 S_3$, corresponding to the oxide, is known. This compound can be produced by heating a mixture of powdered aluminium and sulphur but, like many sulphides of the not-metals, it is readily decomposed by water, yielding the hydroxide of aluminium and hydrogen sulphide:

$$Al_2 S_3 + 6 H_2 O = 2 Al (OH)_3 + 3 H_2 S;$$

from this it follows that when an alkaline sulphide is added to a solution of an aluminium salt, aluminium hydroxide is precipitated, so, for instance, the following reaction takes place between aluminium sulphate and ammonium sulphide:

$$3 (NH_4)_2 S + Al_2 (SO_4)_3 + 6 H_2 O = 2 Al (OH)_3 + 3 (NH_4)_2 SO_4 + 3 H_2 S.$$

A similar reaction takes place when a soluble carbonate is added to the solution of an aluminium salt for, owing to the extreme instability of aluminium carbonate, the hydroxide and not the carbonate is precipitated:

$$3 (NH_4)_2 CO_3 + Al_2 (SO_4)_3 + 6 H_2 O = 2 Al (OH)_3 + 3 (NH_4)_2 SO_4 + 3 H_2 O + 3 CO_2.$$

All of the reactions which have just been mentioned illustrate the weakly basic character of aluminium oxide and hydroxide and show the close relationship existing between aluminium and the not-metals.

CHAPTER XLIX.

GALLIUM, INDIUM AND THALLIUM.

Gallium, Symbol Ga, atomic weight 69; Indium, Symbol In, atomic weight 113.7; Thallium, Symbol Tl, atomic weight 204.18.

Gallium, indium and thallium are very sparingly represented in nature, they are of scarcely any commercial importance so that the interest in them is purely theoretical in its character and is taken because they complete the family of elements of which boron and aluminium are the chief representatives.

Gallium was discovered by Lecocq de Boisbaudran in zinc-blende.* The metal is hard, brittle and crystalline in its structure; it is scarcely malleable or ductile, it melts at 30.15° and is not volatile even at a high temperature; its specific gravity is 5.9. The metal scarcely oxidizes when exposed to the air, and it is readily obtained by electrolysis of a solution of the oxide in alkalis; it decomposes steam and liberates hydrogen (see page 29); like aluminium, it is soluble in hot, caustic alkalis. The chief characteristics of the compounds of gallium are given in the following table:

OXIDES, $Ga\ O$, $Ga_2\ O_3$. The former is the least stable of the oxides, it is basic; the latter is white, infusible; reduced to the metal at white heat by a current of hydrogen. It is both basic and acidic, but dissolves only in the most concentrated caustic alkalis.

HYDROXIDE, $Ga\ (OH)_3$, formed by precipitating the solutions of soluble gallium salts with ammonia water, it is somewhat soluble in an excess of the reagent. When heated, the hydroxide readily loses water and forms the oxide.

CHLORIDES, $Ga\ Cl_2$, $Ga\ Cl_3$. The former is a solid which melts at 164° and boils at 535°; its vapors have a specific gravity which corresponds to a molecular weight represented by the formula $Ga\ Cl_2$. The latter was formerly supposed to have the formula $Ga_2\ Cl_6$ (see page 323), but recent determinations of the specific gravity of the vapors of gallium trichloride shows that body to have a molecular weight corresponding to the formula $Ga\ Cl_3$* at 440°. The trichloride melts at 75.5° and boils at 215° to 220°. It dissolves in water, but when the solution is evaporated it is, in part, changed into the basic chloride, just as was the case with the trichloride of antimony (page 242).

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* Zinc sulphide, $Zn\ S$.

THE SALTS OF GALLIUM are produced by dissolving the hydroxide in the various acids, the sulphate, when evaporated with the sulphates of the alkali metals or of ammonium forms alums. (See page 327).

The discovery of gallium in 1875 was of especial interest because, in the periodic system of the elements as arranged by Mendelejeff a few years previous to that time, an element belonging to the family of which aluminium is a representative was found to be missing.† An element the chemical and physical properties of which should lie between those of aluminium and indium, and which would have an atomic weight of approximately 69, was therefore predicted by Mendelejeff, and this prediction was subsequently brilliantly verified by Lecocq de Boisbaudran.

The next element of this family is indium. Like gallium it occurs in some specimens of zinc-blende. The element was discovered in 1863 by Reich and Richter. It is white, with a metallic lustre lying between that of platinum and silver; it is softer than lead and is very malleable and ductile. Its specific gravity is 7.1; it melts at 176° and it is somewhat volatile at red heat; when heated to redness in the air, it burns to form $In_2\ O_3$. The chief properties of its compounds are given in the following table:

OXIDES, $In\ O$ and $In_2\ O_3$. The former is made by reducing the trioxide in a current of hydrogen; it burns in the air to form $In_2\ O_3$. The trioxide, $In_2\ O_3$, is the most stable oxide of indium, and is the one corresponding to the typical oxide of the family; it is produced when indium is burned in the air or when the hydroxide $In\ (O\ H)_3$ is heated; this latter substance is obtained by precipitation from solutions of indium salts by means of ammonia water. The oxide is easily reduced to the metal by heating the same in a current of hydrogen, the monoxide appearing as an intermediary stage in this reduction. The trioxide and the corresponding hydroxide are mainly basic in their character; they dissolve in acids to form the salts of indium; they are, however, also weakly acidic, for they are dissolved by the hydroxides of potassium or sodium.

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* Nilsson and Petterson, Comptes rendus 107, 572.

† A similar gap was found to exist in the carbon family; this was subsequently filled by the discovery of germanium (see page 298.)

HALOGENE COMPOUNDS, $In\ Cl_2$, $In\ Cl_3$. The latter is formed by the action of chlorine on indium; it sublimes at 440° without melting; its vapor density corresponds to a molecule of the formula $In\ Cl_3$; it dissolves in water without change, but on heating the solution hydrochloric acid passes off and a basic chloride is formed. Indium chloride readily unites with the chlorides of the alkali metals to produce double salts corresponding in formula to those of aluminium (see page 325).

SULPHIDE, $In_2\ S_3$, formed by direct union of indium and sulphur at red heat. A sulphohydrate of indium, $In\ (S\ H)_3$, is precipitated from neutral or weakly acid solutions of indium salts by hydrogen sulphide; in this respect the character of indium approaches that of the most pronounced metals of the preceding (carbon) family.

THE SULPHATE OF INDIUM, when evaporated with the sulphate of an alkali metal or of ammonium, produces an alum (see page 327).

Thallium, the element having the highest atomic weight in this family, was discovered by Crookes in 1861, that investigator finding it in the residues covering the floors of the channels of certain sulphuric acid works; since that time it has been discovered in zinc-blende, iron pyrites and copper pyrites. The metal is white, of crystalline structure and greatly resembles tin; it is malleable and ductile, has a specific gravity of 11.9, melts at 290° and boils at a white heat. Thallium is readily oxidized in the air and dissolves in sulphuric or nitric acid without much difficulty. The high atomic weight of thallium is unfavorable to the expression of a very pronounced chemical character so that, as is the case with lead, it appears with a number of oxides which each, individually, resemble a different group of elements; for instance, the monoxide $Tl_2\ O$ is in its chemical behavior very much like the oxides of the monovalent elements of the alkali family, while the trioxide $Tl_2\ O_3$ falls into line with the similar compounds of the aluminium group. The characteristics of the most important thallium compounds are given below.

OXIDES, $Tl_2\ O$, $Tl_2\ O_3$, $Tl\ O_2$. The first, thallium monoxide or thallous oxide is formed by the slow oxidation of the metal in the air, it is a brownish black powder, *which is soluble in water*, forming the hydroxide $Tl\ OH$, this remarkable solubility shows the resemblance between this oxide and the oxides of the alkali metals, for the latter are likewise soluble in water; a solution of thallous hydroxide has a strongly alkaline reaction, it neutralizes acids to form salts which, for the most part, are soluble in water, (resemblance to the salts of the alkalis, see latter). Thallium trioxide, thallic oxide, formed by heating thallium to a red heat in oxygen, is insoluble in water, the hydroxide $Tl\,O_2\,H$ is formed by precipitating from a solution of a thallium salt by means of ammonia water, neither the oxide nor hydroxide have acidic properties; both are oxidizing agents, having a great tendency to change into thallous oxide, a higher oxide of thallium, $Tl\,O_2$, so-called thallic acid, is also said to exist.

CHLORIDES, $Tl\,Cl$, $Tl\,Cl_3$. The first, thallous chloride, is insoluble in water, is precipitated from solutions of thallous salts by hydrochloric acid and very much resembles the chloride of silver in appearance. (A larger work must be consulted for a description of the thallous salts). The trichloride, $Tl\,Cl_3$, formed by treating thallium with chlorine, is decomposed into thallous chloride and chlorine when heated. Two sulphides of thallium, $Tl_2\,S$ and $Tl_2\,S_3$ are known.

CHAPTER L.

THE DETERMINATION OF ATOMIC WEIGHTS. DULONG AND PETIT'S LAW. THE LAW OF ISOMORPHISM.

The investigations into the gravimetric composition of chemical compounds, which were undertaken at the beginning of the century and which finally developed the laws of definite and multiple proportions, succeeded not only in establishing these purely empirical laws but, as the spirit of inquiry in man leads him to seek a cause behind every regularly recurring phenomenon or law, naturally an explanation for the laws of definite and multiple proportions was looked for and, as we have seen, found in the atomic hypothesis. In spite of the subsequent almost universal acceptance of these laws, some chemists continued to doubt their exactness, indeed, the gravimetric determinations of Dalton's time were too unsatisfactory and varying to inspire much confidence; when, at a later date, Berzelius subjected the work which had been done with the purpose of establishing the laws relating to the definite composition of matter, to a more exact revision and so became a firm believer in their existence, no adequate reason for their non-acceptance by other chemists could be advanced but, when the subsequent discovery of an error in Berzelius's determination of the relative weight with which carbon enters into combination with other elements, shook confidence in all of the established rules, the atomic theory was left in a most unsatisfactory condition, and it was not until 1860 that the painstaking and accurate work of Stas succeeded in showing that the laws of definite and multiple proportions are not merely approximate but are, in reality, mathematically exact. However, the atomic hypothesis had existed in its present form before Stas's time, and it naturally was the endeavor of chemists to determine, not only the mere fact that, for instance, *a* parts by weight of chlorine always unite with *b* parts by weight of silver, they also endeavored, as we have seen in the preceding portions of the work, by calling to their aid various hypotheses and theories of greater or less plausibility, to fix exactly the relative weights of the atoms of silver and chlorine; these atomic weights must necessarily bear such a relationship to each other that, in uniting to form silver chloride, they would always produce that substance with the proportion of *a* parts by weight of chlorine to *b* of silver. As we have seen (page 39) gravimetric determinations alone can do no more than give the relative parts by weight with which two or more substances unite to form a chemical compound; thus, in studying the composition of water by weight, we could but determine that eight parts by weight of oxygen unite with one part of hydrogen; it was only after chemists combined the lesson taught by the gravimetric composition of water with the phenomena attendant on its formation and decomposition, *i. e.*, with the facts that two volumes of hydrogen always unite with one volume of oxygen to form water and that water, when decomposed, always yields two volumes of hydrogen and one of oxygen, and after these experimental facts were explained by Avogadro's hypothesis (page 66 and sub.) that the conclusion was definitely reached that each molecule of water is in reality composed of two atoms of hydrogen united to one of oxygen, by reason of which conclusion the atomic weight of oxygen was fixed at 16 and not at 8.

As has been repeatedly mentioned, the determinations of the specific gravities of gases, provided we accept Avogadro's hypothesis, give us the magnitudes of their molecular weights and, when these are fixed, *provided, in each case the accurate stoichiometric* composition* of the substance in question is known† we can determine the maximum atomic weights of the elements entering into the structure of the molecules of the various gases. (See page 69). The following table, which illustrates the method by which maximum atomic weights are determined from a comparison of the vapor densities of gases, will serve to more clearly fix the method in the mind of the pupil.

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* The relative proportions by weight in which substances unite to form chemical compounds are called the stoichiometric quantities.

† It is evident that the determination of the vapor density of a substance is of no value unless the stoichiometric composition is known. For instance, it is of no influence on the determination of the atomic weight of nitrogen to determine the specific gravity of ammonia and find this to be .589, so that the molecular weight would be 17, we must also know that this 17 parts by weight of ammonia contains 14 parts of nitrogen; when, however, the two facts *are combined*, we can say that the atomic weight of nitrogen cannot be more than 14, for we then know of a substance, the molecular weight of which is not greater than 17, which contains but 14 parts of nitrogen.

Name of gas.	*d.*	*d* x 28.8	*M.*	Analysis by weight.	
Nitric oxide.	1.039	30.	30.03	14.03 nitrogen	+ 16 oxygen.
Nitrogen dioxide.	1.50	43 3	46.03	14.03 "	+ 32 "
Phosphorus trichloride.	4 88	140.9	137.35	31 phosphorus	+ 106.35 chlorine.
Phosphorus tri-iodide.	14.46	417.1	411.55	31 "	+ 380.55 iodine.
Hydrochloric acid.	1.247	36.	36.457	1.007 hydrogen	+ 35.45 chlorine
Hydroiodic acid.	4.443	128.	127.857	1.007 "	+ 126.85 iodine.
Water	0.623	17.99	18.014	2.014 "	+ 16 oxygen.
Sulphur dioxide.	2.247	64.9	64.06	32.06 sulphur	+ 32 oxygen.

In this table *d* is the specific gravity, air = 1; *d* x 28.8 is the specific gravity, H = 2;* *M* is the molecular weight, found by adding the figures given in the last column.

After a study of the above table we can see that, were chlorine, for example, to occur in but one compound, and that one the trichloride of phosphorus, evidently the atomic weight of the element would be placed at a maximum of 106.35; it could be no greater, for the molecular weight of the chloride of phosphorus is known. However, if we glance further down the column, we discover hydrochloric acid with a molecular weight of 36.457; each molecule of this contains but 35.45 parts by weight of chlorine; it follows therefore that the weight of 106.35, which is the amount of chlorine contained in the chloride of phosphorus, really represents *three atoms of chlorine,* provided the molecule *of hydrochloric acid contains but one of these.* The number 35.45 must therefore be fixed upon as the atomic weight of chlorine, and must remain so, unless, at some future time, we were to discover a compound of chlorine, the molecular weight of which is known and which contains *less than this quantity.* In the latter event, a molecule of hydrochloric acid would necessarily contain *more than one atom of chlorine.* Similar considerations will help us to select the number 126.85 as representing the atomic weight of iodine, while a comparison of the figures in the table given above will further show us that by means of the determinations even of the very few substances mentioned there, the maximum atomic weights of nitrogen, phosphorus, sulphur, oxygen, chlorine and iodine are given. These same methods of investigation have been applied in every case where the study of elements and compounds in the gaseous state has been possible, so that the maximum atomic weights of the greater number of elements have been ascertained with reasonable certainty.

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* The specific gravity of air. H = 2, is 28.8, hence specific gravities taken with air as unity are converted to these with H = 2 by multiplying wth 28.8.

The determination of the specific gravities of gases, although by far the most important, is not the only method for ascertaining molecular weights. In 1882, F. M. Raoult demonstrated that aqueous solutions of organic substances, provided they contain the dissolved compounds in quantities proportional to their molecular weights, have identical freezing points, and subsequently the same law was found to hold good for other substances as well, although the amount of depression differs for each solvent. If Δ is the lowering of the freezing point of a solvent, brought about by the solution of n molecular weights of a certain substance in g grams of the solvent then:

$$1.\quad \Delta = r\frac{n}{g},$$

where r is a constant depending only on the nature of the solvent. When the molecular weight of the substance is not known, this can be ascertained by experimentally determining the lowering of the freezing point of the solvent brought about when p grams of the substance are dissolved in g grams of that solvent for then $n = \frac{M}{p}$, where M is the molecular weight, so that equation 1, becomes:

$$2.\quad \Delta = \frac{r\,p}{M\,g}, \text{ or,}$$

$$3.\quad M = \frac{r\,p}{\Delta\,g}.$$

The constant, r, can be determined once and for all, for any given solvent, by dissolving one or two substances of known molecular weight therein, and observing the depression of the freezing point for, from equation 1,

$$r = \frac{\Delta\,g}{n.}$$

The objection to this method of determining molecular weights lies in the fact that it is applicable only in the limited number of cases where substances are soluble in a medium which is capable of being frozen at a convenient temperature while, furthermore, the law has not held good in a number of cases which have been observed. The application of this method is, nevertheless, very valuable to confirm molecular weights determined by some other means, and to ascertain the same in many cases where the determination of the specific gravities of gases is impracticable. Similar methods, based upon the lowering of the vapor pressure of solutions by reason of dissolved substances, have also been applied to the determination of molecular weights, for their study the pupil must refer to some text-book more especially devoted to these subjects.*

The atomic weights which, by the application of Avogadro's hypothesis (page 66) and the determinations of the vapor densities of elementary and compound substances, have been selected as those which really represent the relative weights of the individual atoms, would be much more worthy of confidence if other physical measurements would, when correctly interpreted, indicate that this selection had been properly made. Such an aid is found in the application of a law discovered by Dulong and Petit in the early part of this century. Those two investigators proved that the greater the combining weight of any given element was found to be, the less was the specific heat (capacity for heat) of that element in the solid form, so that the *product of the combining weight of any given element and its specific heat was found to be very nearly equal to the same product for any other element.* This law is susceptible of a very simple physical explanation. The specific heat of a body is the quantity of heat necessary to increase the temperature of the *unit weight* of that body by 1°, it follows that the product of the specific heat and the combining weight of an element represents the quantity of heat necessary to warm that weight through 1°, if we select as the combining weights of the elements *those numbers which, by using Avogadro's hypothesis,* we have decided upon as being the atomic weights, then the above mentioned product is very nearly 6.4 in the great majority of cases; this product can be termed the "atomic heat" of the elements so that Dulong and Petit's law assumes the following simple form:

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*Ostwald, Outlines of General Chemistry, Walker's translation.

The atomic heats (capacities for heat of the individual atoms) of all elements are very nearly equal.*

This law is without exception with all true (ductile) metals, is true for almost all metals which, like antimony or tin, also have not-metallic properties (which are brittle but which have metallic lustre) and also holds good for the greater number of not-metals. A few examples will serve as an illustration.

Element.	c.	a.	a. c.	
Lithium.	.941	7.02	6.6	In this table. c = specific heat. a = atomic weight. ac = atomic heat.
Magnesium.	.250	24.3	6.07	
Chromium.	.121	52.1	6.3	
Iron.	.114	56.	6.38	
Cobalt.	.107	59.	6.3	
Nickel.	.108	58.7	6.3	
Bromine.	.084	79.95	6.7	
Gold.	.032	197.3	6.3	

If we are acquainted with an element, therefore, the maximum atomic weight of which we have never been able to determine by means of the vapor densities of some of its compounds, we can, as a next resort, select as its true atomic weight that stoichiometric quantity which, when multiplied by the specific heat of the element in question, will give us a number approximately equal to 6.4. Of course, were no method for fixing atomic weights as valuable as that given us by the determinations of the specific gravities of the gases available, this law of Dulong and Petit would lead to no definite results; for it is obvious, when we consider the above table, that were we to select as atomic weights numbers exactly one-half as large as those given above, the product a. c. would still remain constant and would be approximately equal to 3.2, so that only when, by the use of other physical and chemical means, we have definitely decided that in the case of a number of elements that product must be 6.4 and not 3.2, then it follows that in all undetermined cases the atomic weights must be nearly equal to the quotients of $\frac{6.4}{c}$. Naturally, the numbers so obtained are not the exact atomic weights; they can only be close enough to the true numbers to show that the atomic weights to be selected are not one-half or twice or three times the stoichiometric quantities which come closest to those indicated by dividing 6.4 by the respective specific heats.

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*For a more extended exposition of the results obtained by Dulong and Petit's law, see Lothar Meyer, Die Grundzüge der Theoretischen Chemie, Leipzig, 1890.

The few marked exceptions to Dulong and Petit's law are not calculated to give any great difficulty for, in the cases where they occur, the elements in question form a number of gasifiable compounds, and consequently there is no reason why the specific gravities of these compounds should not definitely fix their maximum atomic weights. One example of such an exception will serve to illustrate this conclusion. The chemical equivalent weight of carbon is 3,* its specific heat as diamond is 1.47, as graphite 1.98. The atomic weight of carbon must be some rational multiple of its equivalent weight so that, according to the rule, we must select a number as the atomic weight of carbon which, being a rational multiple of the equivalent weight, will, when multiplied by the specific heat of carbon, give a product approximately equal to 6.4. This product is reached in the case of diamond when we take fourteen times the equivalent weight, and therefore it would follow that the atomic weight of carbon is 42; in the case of graphite, however, we would come to a different result, for then $a. c = 6.5$ when $a = 33$. These atomic weights are entirely impossible, however, for we are acquainted with a number of carbon compounds in which (the vapor density and hence the molecular weight being known) we have only 12 parts by weight of carbon, so that there remains no alternative but to believe that carbon presents an exception to Dulong and Petit's law. However, the specific heat of carbon is much greater at high temperatures than it is at low ones, at 900° it is .459 ($a. c$ would then be equal to to 5.51). so that at a white heat carbon would probably follow Dulong and Petit's law. These facts make it apparent that specific heat determinations are of no value in the selection of atomic weights unless they are made through *large intervals of temperature, and are then found to be constant.* Boron, silicon, beryllium, phosphorus and sulphur have, like carbon, very small specific heats. These elements, which are exceptions to Dulong and Petit's law, have small atomic weights and are, all but beryllium, not-metals.

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* By the chemical equivalent weight of an element is meant that quantity of the element which will enter into combination with one part by weight (one atom) of hydrogen or which will take the place of one atom of hydrogen in a chemical compound. The equivalent weight of carbon is 3, because three parts by weight of carbon unite with one of hydrogen. The atomic weight of carbon is $4 \times 3 = 12$, for the simplest hydrogen compound of carbon is $C\,H_4$.

Dulong and Petit's law is applicable in other cases besides those in which the specific heats of solid elements are to be considered, for *as the capacity for heat of a solid compound is very nearly equal to the sum of the capacities of its constituent parts,* it is evident that in many cases the individual atomic heats can be obtained by a determination of the specific heats of compounds. This method is especially useful in cases where the elements themselves are not to be obtained as solids; for example:

Silver; atomic weight, 107.9; specific heat, .056; a c = 6.04
Iodine; " " 126.8; " " .054; a c = 6.8

The sum of the atomic heats of silver and iodine = 12.84

The *observed* specific heat of silver iodide is .061. This, multiplied by the sum of the atomic weights of silver and iodine, gives 14.3, a number which is but little greater than the one calculated above, namely 12.84. The same is the case with silver bromide, for:

Silver; atomic weight, 107.9; specific heat, .056; a c = 6.04
Bromine; " " 79.9; " " .084; a c = 6.7

Calculated for Ag Br = 12.8
Silver bromide; formula weight, 187.8; specific heat, .074; a c = 13.9

The two examples given above show us, therefore, that in the case of substances the formulæ of which are made up of two atomic weights, the capacity for heat of the formula weight of the compound is very nearly equal to twice that of either of the individual atoms, and further investigation would demonstrate that compounds made up of three atomic weights ($Pb\ Br_2$ and $Pb\ I_2$) have about three times the capacity of each individual atom. Having settled, by experimental evidence, that Dulong and Petit's law hold's good for compounds, all of the constituent parts of which can be obtained in the solid state, we can extend the method so as to indirectly determine the atomic heats of elements which are gases at any temperature which permits of a detailed study of their properties. For example, we wish to discover the atomic heat of chlorine:

Silver chloride; formula weight, 143.35; specific heat, .091; a c = 13
Silver; atomic weight, 107.9: " " .056; a c = 6.04

Capacity for heat of 35.45 parts of chlorine = 6.96

The difference, 6.9, obtained as the atomic heat of chlorine is, however, very close to the average of 6.4 which is found by direct observation in a large number of solid elements, so that if we regard as the true atomic weight of chlorine the number 35.45, which is taken by reason of a large number of specific gravity determinations of gasifiable chlorine compounds, the atomic heat of that element very nearly coincides with the numbers obtained by direct observation on a large number of solid elements, and it therefore follows that the maximum atomic weight of 35.45 is confirmed by an application of Dulong and Petit's law. Applications of this method with other elements which, like chlorine, have such low melting points that their respective specific heats cannot be measured when they are in the solid state, have led to like results, although there are a few exceptions, nearly all of which belong to compounds containing not-metals with small atomic weights.*

Dulong and Petit's law helps us to confirm numbers already decided upon as atomic weights, and when a decision has been reached in regard to a large number of elements by using some other method as a guide, it can then help us to determine which numbers, representing multiples or simple fractions of the equivalent weights, are the true atomic weights of elements which form no gasifiable compounds and which are themselves not volatile. In no case can the law be of assistance in determining molecular weights.

A third method which has been of use in determining the numbers to be selected as atomic weights has been a study of the laws of isomorphism. In 1819 Mitscherlich discovered that certain elements can replace others in chemical compounds without thereby materially altering the crystalline forms of those compounds. These, as well as the elements replacing each other in them, are said to be *isomorphous* (see page 42). The replacing of one element by another always takes place in definite stoichiometric quantities; for example, in the isomorphous group, $NaCl$, $NaBr$, NaI, 35.45 parts by weight of chlorine are always replaced by 80 parts of bromine and 126.85 parts of iodine, and it is very evident that, *provided the atomic weight of one of these elements has been decided upon by some other method*, the atomic weights of the others will be given by the stoichiometric quantities which replace that element without altering the crystalline farm, provided that *in isomorphous mixtures elements*

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* Compounds of hydrogen, nitrogen, fluorine, oxygen.

replace each other atom for atom, and this is the case with the vast majority of isomorphous compounds.[*] This method for determining atomic weights becomes very far reaching when we consider that the same element may belong to two or three isomorphous groups of compounds, so that when a decision as to the atomic weights of the elements in one of these groups has been arrived at, we can then cross over to another and perhaps in that one discover an element which also belongs to two or three new isomorphous groups, and so on. It follows, therefore, that *the selection of the atomic weight of an element according to some other method* may lead to the determination of the atomic weights of a large number of others. For example, the atomic weight of zinc, obtained by a determination of the vapor density of some of the compounds of that element which can be studied as gases,[†] has been placed at 65.3. This proportional part by weight of zinc when crystallized in the sulphate is, however, replaced by:

58.7 parts of nickel; 56 parts of iron;
59. " " cobalt; 55 " " manganese and
24.3 parts of magnesium.

Iron, manganese and magnesium are further isomorphous with 40 parts of calcium on the one hand and with 27 parts of aluminium and 52.1 parts of chromium on the other. Now, 40 parts of calcium can replace 87.6 parts of strontium, 137 parts of barium and 206.95 parts of lead, so that the selection of the maximum atomic weight of zinc can bring about the determination of a large number of other atomic weights. In using the law of isomorphism one fact must, however, be born in mind, namely, a number of instances are known in which groups of atoms can replace individual atoms isomorphously, as is the case with ammonium and potassium salts, where the radicle NH_4 takes the place of the atom K, and if this can be true of ammonium and potassium it is without doubt true of a large mental facts have been considered, the maximum atomic weights which are selected by the method brought about by Avogadro's hypothesis have been universally accepted as the basis of our present system. This solution seems to be the correct one when we remember that only these atomic weights, when arranged in order, beginning with that belonging to the element with least atomic weight and ending with that with the greatest, form a natural system in which elements with similar properties recur after stated intervals. This arrangement, known as the periodic system of the elements, will be discussed in the next chapter.

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[*] Mere similarity or even identity of crystalline form, even where two bodies showing such similarity or identity are similarly constituted, does not mean *that the bodies in question are isomorphous*. In order to conform with the laws of isomorphism they must be able to replace each other without thereby materially altering the form of the crystal. Such isomorphous compounds are the alums (page 327), the vitrols (see magnesium), the calcite and arragonite groups of carbonates (see page 281).

[†] For example, zinc ethyl, $Zn(C_2H_5)_2$.

CHAPTER LI.

THE PERIODIC SYSTEM OF THE ELEMENTS.

In our previous discussion of chemistry we have regarded the properties of compounds as being the properties of the molecules which, when massed together, make up those compounds, and we have also learned that the character of any individual molecule depends on the nature of the atoms which, in uniting, produce that molecule. If we wish to systematically study the connection between the characters of elements and their compounds, we must first attempt to compare the fundamental constants which appertain to the atoms and which are definitely determinable and to be ascertained with great accuracy. Such constants are the atomic weights and the specific gravities of elementary bodies.

In the year 1868 both Mendelejeff and Lothar Meyer demonstrated that, when the elements are arranged in the order of their increasing atomic weights, each element will differ in properties from those immediately preceding and following it, but nevertheless after certain definite intervals elements will recur which possess very similar characteristics. This interval they found to be after every seventh element in the first fourteen, and after every seventeenth in the remainder of the series. The elements were therefore divided into two "short periods" of seven each, and into five "long periods" of seventeen individuals. The periods being so selected that each begins with an alkali metal and ends with a halogene; for by this arrangement the extremities are formed if sharply contrasting elements. The long periods are, however, in reality double, for in each one the first seven elements resemble the last seven in many important chemical characteristics, while the three remaining elements which are in the middle* form a separate group.

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*Elements No. 8, 9 and 10 of any long period.

The arrangement of the elements in the periodic system, including the division into short and long periods, is shown in the following table:

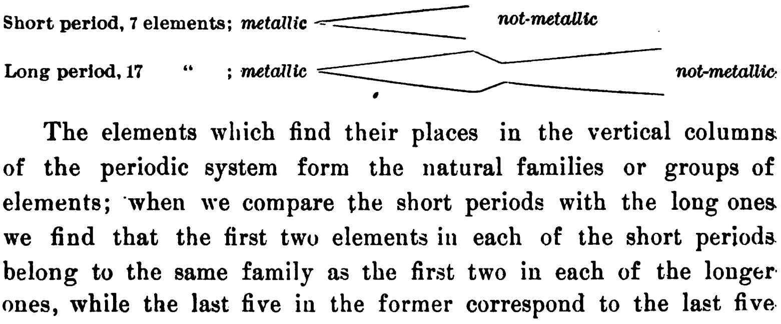
Li 7.02	Be 9	B 11	C 12	N 14.03	O 16	F 19
Na 23.05	Mg 24.3	Al 27	Si 28.4	P 31	S 32.06	Cl 35.45

K 39.11	Ca 40	Sc 44	Ti 48	V 51.4	Cr 52.1	Mn 55	Fe 56	Co 59	Ni 58.7	Cu 63.4	Zn 65.3	Ga 69	Ge 72.3	As 75	Se 79	Br 79.95
Rb 85.5	Sr 87.6	Y 89.1	Zr 90.6	Cb 94	Mo 96	—	Ru 101.6	Rh 103.5	Pd 106.6	Ag 107.92	Cd 112	In 113.7	Sn 119	Sb 120	Te 125	I 126.85
Cs 132.9	Ba 137	La 138.2	Ce 140.1	Di 142.3	—	—	—	—	—	—	—	—	—	—	—	—
—	—	Yb 173	—	Ta 182.6	W 184	—	Os 191.7	Ir 193.1	Pt 105	Au 197.3	Hg 200	Tl 204.18	Pb 206.9	Bi 208.9	—	—
—	—	—	Th 232.6	—	U 239.6	—	—	—	—	—	—	—	—	—	—	—

The very rare elements, Samarium, 150, Terbium, 159.5, and Erbium, 166.3 have been omitted from this table, as their properties are too little known to be the basis of generalization

The first two (short) periods and the third and fourth (long) periods are complete with one exception, an element with an atomic weight of about 100 and corresponding to manganese. The remaining periods only have a few known representatives in each, and all of those, with possibly one or two exceptions, can be classed with the very rare elements. As a consequence, all generalizations must be made from a study of the complete periods, while the conclusions drawn from the latter can only be cautiously extended so as to cover the ones in which a number of representatives are missing.

The short periods are the types of all; the others are constructed after those models with this exception:—While the short periods, beginning as they do with a pronounced metal and ending with a pronounced not-metal, will show all gradations of character which lie between those two extremes while traversing the five intervening elements, the long periods, although they begin and end each with an equally pronounced metal and not-metal, nevertheless require the interposition of fifteen elements to effect the gradation which is produced by five in the short periods; and from this it follows that the elements in the middle of the long periods must be further removed in character from those in the middle of the short periods than are the elements at either extremity; we would therefore expect elements like chromium, manganese, iron, cobalt, nickel and copper to have no counterparts in the typical periods. This conclusion is not strictly correct, however, for, as has been mentioned, the long periods are really each composed of two shorter ones. The last members of the first half of the long periods therefore resemble in many ways the last members of the typical short periods, while the first elements of the second half are much like the elements which begin the short periods. Any given long period begins with a most pronounced metal like potassium or caesium; following this are six elements each one of which is less metallic in its nature than the one immediately preceding it; the eighth, ninth and tenth elements then form a transition from the first to the second seven of the long period; they are successively *more* metallic in their nature. The eleventh element is once more a tolerably pronounced metal, although it has by no means so metallic a nature as the alkali metals which begin a period. From the eleventh to the seventeenth element the not-metallic properties again become more and more pronounced, until the last elements of the periods (bromine or iodine) are among the most intensely not-metallic elements with which we are acquainted. The gradation in properties shown by the periods can, perhaps, be graphically represented as follows:—


Short period, 7 elements; *metallic*
not-metallic
Long period, 17 " ; *metallic*
not-metallic

The elements which find their places in the vertical columns of the periodic system form the natural families or groups of elements; when we compare the short periods with the long ones we find that the first two elements in each of the short periods belong to the same family as the first two in each of the longer ones, while the last five in the former correspond to the last five in the latter; as has been pointed out, the intervening ten elements in the long periods differ more or less from any which occur in the typical periods. This relationship is clearly shown by the following table:

Li,	Be,											B,	C.	N,	O,	F,
Na,	Mg,											Al,	Si,	P,	S,	Cl,
K,	Ca,	Sc,	Ti,	V,	Cr,	Mn.	Fe,	Co,	Ni,	Cu,	Zn.	Ga,	Ge.	As,	Se,	Br,
Rb,	Sr.	Y,	Zr.	Cb,	Mo,	—,	Ru,	Rh,	Pd.	Ag,	Cd.	In,	Sn.	Sb,	Te,	I,
Cs,	Ba.	La.	Ce,	Di.	—,	—,	—,	—,	—,	—,	—.	—,	—.	—,	—,	—,
		Yb,	—.	Ta,	W,	—,	Os,	Ir,	Pt,	Au,	Hg	Tl,	Pb.	Bi,	—,	—,
			Th.	—.	U.	—,										

As we pass from member to member along the complete series of the elements we encounter, at one time, a gradual, at another an abrupt change in the character of the elements; the gradual changes between the two extremities of any period, the abrupt changes as we pass from one period to another, and these changes are brought about, with close resemblance in each one of the periods, so that nearly every property of any given element is repeated in one or more subsequent ones; this repetition is found, not only in the chemical character of the elements and their compounds, but is also apparent, even in a greater degree, in their physical properties, *the properties of any individual element are therefore determined by the position of that element in the periodic system.*

One of the constants which appertains to each element is its specific gravity in the solid state, and that regularly increases and decreases as we pass from element to element in each one of the periods. This fact becomes very apparent if, instead of comparing the specific gravities themselves, i. e., the quantities of matter contained in the unit volume, we compare the *volumes* which are occupied by weights of the respective elements which are so taken as to correspond to the atomic weights. By this means we can arrive at the volumes occupied, in each case, by the same number of atoms, which, necessarily, must bear the same relationship to each other as the volumes occupied by the individual atoms; these volumes can appropriately be termed "atomic volumes," and are to be readily ascertained in each case by dividing the atomic weight by the specific gravity, so that:

$$V = \frac{a}{c},$$

Where V represents the atomic volume, a the atomic weight and c the specific gravity of the solid element; for instance, the atomic weight of lithium is 7.02, its specific gravity is .59, its atomic volume is therefore $\frac{7.01}{.59} = 11.9$; the quotient 11.9 means that 7.01 grams of lithium occupy 11.9 cubic centimeters of space; the atomic weight of manganese is 55, its specific gravity is 8, its atomic volume 6.9, therefore 55 grams of manganese take up 6.9 cubic centimeters. The following table demonstrates the relationship between the atomic volumes and the periodic system:

Li	Be	B	C	N	O	F
c = .59	1.85	2.68	3.3	3?	2?	1.5?
v = 11.9	4.9	4	3.6	5	8	13.
Na.	Mg	Al	Si	P	S	Cl
c = .97	1.74	2.56	2.49	2.3	2.04	1.38
v = 23.7	13.9	10.6	11.4	13.5	15.7	25.6

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
c = .86	1.57	2.6	3.7	5.5	6.8	8	7.8	8.5	8.8	8.9	7.15	5.96	5.47	5.67	4.6	2.97
v = 45.4	25.4	17.	13.	9.3	7.7	6.9	7.2	6.9	6.7	7.1	9.1	11.7	13.2	13.2	17.1	26.9
Rb	Sr	Y	Zr	Cb	Mo	—	R	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
c = 1.52	2.50	3.6	4.15	7.06	8.6	—	12.26	12.1	11.5	10.5	8.65	7.42	7.29	6.76	6.25	4.94
v = 56.2	35.	24.8	21.8	13.3	11.1	—	8.1	8.4	9.1	10.1	12.8	15.4	16.3	17.9	20.	25.6

In each period, whether it be short or long, the specific gravity begins with a minimum (with the specifically light alkali metals) advances to a maximum at the middle and then, once more, diminishes to a minimum at the opposite, not-metallic extremity, each period, therefore, represents a complete wave in regard to specific gravites, the beginning being in the trough, the middle at the crest, and the end in the succeeding trough; the reverse is true in regard to atomic volumes, these begin with their maximum at the alkali metals, diminish to a minimum at the center of the periods, and then once more increase to a maximum at the other extremity; the changes in the atomic volumes in each period, therefore, may be compared to a wave the crest of which corresponds to the beginning alkali metal, the trough to the middle of the period and the succeeding crest to the next following alkali metal. The atomic volumes of the alkali metals, however, increase rapidly with increasing atomic weight, so much so, indeed, that the atomic volume of sodium is twice that of lithium, and the atomic volume of potassium is twice that of sodium; each succeeding wave which represents the changes in the atomic volumes of the elements forming one period has *a greater amplitude* than the one preceding it, and a lesser amplitude than the one following. If, then, we take the atomic volumes as our guide, representing these as ordinates and the atomic weights as abscissæ, we can represent the periodic system in the form of successive wave-like curves, the relative position of any element upon these curves determines the properties of that element. Those elements which find their places on a descending branch of one of these curves and which immediately follow a maximum, and the next following elements down to a minimum and even a little beyond this point, are difficult to fuse, and are not volatile and, furthermore, they are less fusible the nearer they approach a minimum; those elements in the ascending curves are easily melted and, with few exceptions, are volatile; of the elements belonging to the latter class, nitrogen, oxygen and fluorine in the first period are gases, in the second, chlorine only is a gas, phosphorus and sulphur, however, melt at a low temperature and are easily volatilized, in the first long period the volatile elements begin with zinc, in the next following with silver and in the next (incomplete) one with mercury. Lothar Meyer, in consideration of these facts has established the following rule. In that portion of the series in which the atomic volumes are *decreasing with increasing atomic weights*, the elements are not volatile and fusible with difficulty, on the other hand, where the atomic volumes are *increasing* the elements are easily melted and volatile. All of the other properties of the elements vary twice in each of the long periods, so, for instance, the alkali metals at the maxima of the curves as well as the metals immediately following are malleable and ductile, then, as the minima are approached, there follow brittle, crystalline metals, these, in turn, at the minima give way to malleable and ductile ones, and succeeding the latter, as the next maximum is approached, the not-metals, which are neither malleable nor ducticle find their places.

If we designate as positive those elements whose oxides, in the greater number of cases, act as bases, and as negative, those elements whose oxides are anhydrides,* then the periods each begin with strongly positive alkali metals, next following, on descending curves of the atomic volumes, are a number of less positive elements, as a minimum is approached the latter give way to one or two negative, or at least in greater part negative, individuals; succeeding these, at the minimum and at the beginning of the ascent toward the maximum are a number of positive elements and finally the curves are completed by elements which are entirely negative.

That the chemical properties of the elements are altogether in harmony with the periodic system has been repeatedly noted as certain sections have been discussed during the progress of this work and, as the relationships have already been discussed at length when the various families have been taken up and as they will be further noted in those which are to come, it seems scarcely necessary at this place to do more than to briefly state some few connections.

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* See page 12.

By determining the specific gravities of the gases obtained by volatilizing the halogene and hydrogen compounds of the elements, we are able to determine the respective valences of the atoms (see page 103). If we compare the halogene and hydrogen compounds in the first period with those in the second, we find the changes in valence, as we go from left to right, to be identical in both. The beginning elements (alkali metals) are invariably univalent. Passing from these to the right, we find that the valence is increased by one with each pair of successive elements until a maximum of four is reached in connection with the members of the carbon family; it then successively diminishes until it once more reaches a minimum of one (halogene family). These changes are made apparent by the following table:

(R represents an atom either of hydrogen or of chlorine.)[*]

	Li,	Be,	B,	C,	N,	O,	F,
Compounds,	Li R,	Be R_2,	B R_3	C R_4,	N R_3,	O R_2,	F R,
Valence,	1,	2,	3,	4,	3,	2,	1,
	Na,	Mg,	Al,	Si,	P,	S,	Cl,
Compounds,	Na R,	Mg R_2,	Al R_3,	Si R_4,	P R_3,	S R_2,	Cl R.

A different result becomes apparent in comparing the compounds of the elements with oxygen. The valence toward that element (page 105) begins with one in the family of the univalent alkali metals and increases to a maximum of seven with the halogenes. This change becomes evident if we represent a single valence of one of the atoms of oxygen by r, $O = 2r$, and then group the elements as shown in table:

	Li,	Be,	B,	C,	N,	O,	F.
Oxides,	Li_2O,	Be O,	B_2O_3,	CO_2,	N_2O_5,	—	—
	Li r,	Be r_2,	B r_3,	C r_4,	N r_5,	—	—
	Na,	Mg,	Al,	Si,	P,	S,	Cl.
Oxides,	Na_2O,	Mg O,	Al_2O_3,	SiO_2,	P_2O_5	SO_3,	(Cl_2O_7)
	Na r,	Mg r_2,	Al r_3,	Si r_4,	P r_5,	S r_6,	Cl r_7
Valence,	1,	2,	3,	4,	5,	6,	7,

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[*] This comparison is legitimate only in the first two periods, and then with the understanding that, where a hydrogen compound of an element does exist, we study that substance and not the chloride.

In making this comparison we must remember that carbon, nitrogen, phosphorus, sulphur and chlorine each form a number of oxides, so that it is only in those compounds which contain the greatest amount of oxygen that the elements in a short period present a regular increase of valence from one to seven. In the long periods there are but few hydrogen compounds, and these belong only to the last few elements of the periods, so that if we wish to compare the long periods with the short ones, we will be compelled to resort almost exclusively to the chlorine compounds. If the halides of the elements in the short periods were to exactly correspond to the hydrogen compounds, we would be able to construct the following table:

Hydrogen compounds,	$N H_3$,	$O H_2$,	$F H$.
	$P H_3$,	$S H_2$,	$Cl H$.
Halogene compounds,	$N Cl_3$,	$O Cl_2$,	$F Cl$,
	$P Cl_3$,	$S Cl_2$,	$Cl Cl$.

All of these chlorine compounds do, in reality, exist, but, in addition, phosphorus is able not only to form a trichloride, $P Cl_3$, but also a pentachloride, $P Cl_5$, while sulphur presents a tetrachloride, $S Cl_4$, a dichloride, $S Cl_2$, and a monochloride, $S_2 Cl_2$; and the difficulty of a systematic comparison of the halides is further enhanced by the discovery in the long periods of chlorides having the formula $Mo Cl_5$ and $W Cl_6$. From these facts we are, perhaps, justified in drawing the conclusion that, probably, in the two short periods the valence toward chlorine would increase from one to seven, just as it does toward oxygen, if it were not for the fact that the not-metallic elements in those periods are too negative to enable them to retain any great number of chlorine atoms in a stable molecule. This objection does not appertain to the more metallic elements like molybdenum and tungsten, which belong to the same families and which follow, for with these, as the above formulæ show, the valence toward chlorine can be five and six. The double nature of the long periods is once more plainly demonstrated by the valence toward oxygen of the elements belonging therein. The initial alkali metal is always univalent; advancing from this the valence steadily increases with each successive element until a maximum of seven is reached; it then diminishes in the eighth, ninth and tenth, is again equal to one in the eleventh, and from this to the seventeenth once more increases to a maximum of seven. In order to illustrate these changes, we will select the first one of the long periods and, in order to more clearly demonstrate the existing resemblance between its first and second halves, will place the one under the other:

	K,	Ca,	Sc,	Ti,	V,	Cr,	Mn,	Fe,	Co,	Ni,
Oxides,	$\mathrm{K_2O}$,	CaO,	$\mathrm{Sc_2O_3}$	$\mathrm{TiO_2}$,	$\mathrm{V_2O_5}$.	$\mathrm{CrO_3}$,	$\mathrm{Mn_2O_7}$,	$\mathrm{FeO_3}$,	$\mathrm{CoO_2}$,	$\mathrm{Ni_2O_3}$
	$\mathrm{K}\,r$,	$\mathrm{Ca}\,r_2$,	$\mathrm{Sc}\,r_3$,	$\mathrm{Ti}\,r_4$,	$\mathrm{V}\,r_5$,	$\mathrm{Cr}\,r_6$,	$\mathrm{Mn}\,r_7$,	$\mathrm{Fe}\,r_6$,	$\mathrm{Co}\,r_4$,	$\mathrm{Ni}\,r_3$,
	Cu,	Zn,	Ga,	Ge,	As,	Se,	Br,			
Oxides,	$\mathrm{Cu_2O}$,	ZnO,	$\mathrm{Ga_2O_3}$.	$\mathrm{GeO_2}$,	$\mathrm{As_2O_5}$,	$\mathrm{SeO_3}$,	$(\mathrm{Br_2O_7})$			
	$\mathrm{Cu}\,r$,	$\mathrm{Zn}\,r_2$,	$\mathrm{Ga}\,r_3$,	$\mathrm{Ge}\,r_4$,	$\mathrm{As}\,r_5$,	$\mathrm{Se}\,r_6$,	$\mathrm{Br}\,r_7$.			

The elements in the first half of this long period, beginning as they do with the very intensely metallic alkali metal and ending with a metal (manganese), are necessarily much more positive than those of the second half which end with a pronounced not-metal (bromine), yet, nevertheless, the two sections bear a striking resemblance to each other. This long period can therefore be said to be formed of a primary and secondary short period and of the three elements, iron, cobalt and nickel, which connect the the two halves and form a gradual transition from one to the other. Both the *primary and secondary short periods resemble the typical short periods.* This relationship is made more apparent in the following table, which is the one in general use:

	1	2	3	4	5	6	7	8
	H = 1.007							
2.	Li 7.02	Be 9	B 11	C 12	N 14	O 16	F 19	
3.	Na 23	Mg 24.3	Al 27	Si 28.4	P 31	S 32	Cl 35.5	
4.	K 39	Ca 40	Sc 44	Ti 48	V 51.4	Cr 52	Mn 55	Fe Co Ni 56 59 58.7
5.	Cu 63.4	Zn 65.3	Ga 69	Ge 72.3	As 75	Se 79	Br 80	
6.	Rb 85.5	Sr 87.6	Y 89	Zr 90.6	Cb 94	Mo 96	—	Ru Rh Pd 101.6 103.5 106.6
7.	Ag 108	Cd 112	In 113.7	Sn 119	Sb 120	Te 125	I 126.8	
8.	Cs 132.9	Ba 137	La 138	Ce 140	Di 142.3	—	—	— — —
9	—	—	—	—	—	—	—	
10	—	—	Yb 173	—	Ta 182.6	W 184	—	Os Ir Pt 191.7 193.1 195
11	Au 197.3	Hg 200	Tl 204	Pb 207	Bi 209	—	—	
12	—	—	—	Th 232.6	—	U 239.6		

The elements which are placed between the vertical lines constitute the natural families, those in the horizontal lines are the periods or series, those periods which have even numbers constitute, with the exception of the first short period, the first sections of the long periods, those with the odd numbers, with the exception of the second short period (number 3) form the second sections, the series having even numbers, therefore, bear the closest resemblance to each other, while those having odd numbers also show a great similarity of characteristics, on the other hand, the periods numbered with odd numbers bear a much less marked resemblance to those with even ones. These peculiarities will be demonstrated more at length during the discussion of the individual families of metals. If a table of the oxides of the elements is constructed, while following out the arrangement given above, the remarkable regularity displayed in the formation of those compounds is made apparent.

2.	Li_2O,	Be_2O_2,	B_2O_3,	C_2O_4,	N_2O_5,	—,	—,
3.	Na_2O,	Mg_2O_2,	Al_2O_3,	Si_2O_4,	P_2O_5,	S_2O_6,	Cl_2O_7,
4.	K_2O,	Ca_2O_2,	Sc_2O_3,	Ti_2O_4,	Y_2O_5,	Cr_2O_6,	Mn_2O_7,
5.	Cu_2O,	Zn_2O_2,	Ga_2O_3,	Ge_2O_4,	As_2O_5,	Se_2O_6,	Br_2O_7,
6.	Rb_2O,	Sr_2O_2,	Y_2O_3,	Zr_2O_4,	Cb_2O_5,	Mo_2O_6	—,
7.	Ag_2O,	Cd_2O_2,	In_2O_3,	Sn_2O_4,	Sb_2O_5,	Te_2O_6,	I_2O_7,
8.	Cs_2O,	Ba_2O_2,	La_2O_3,	Ce_2O_4,	Di_2O_5,	—,	—,
9.	—,	—,	—,	—,	—,	W_2O_6,	—,
10.	—,	—,	Yb_2O_3,	—,	Ta_2O_5,	—,	—,
11.	Au_2O,	Hg_2O_2,	Tl_2O_3,	PbO_4,	Bi_2O_5,	U_2O_6,	—,
12.	—,	—,	—,		—,		

In constructing this table the formulæ of the oxides in the families of beryllium, carbon and sulphur have been doubled, so as ~~to render the increase~~ in the valence toward oxygen, as the series proceed from left to right, more apparent. Of course, a number of the elements form oxides with formulæ differing from those given in the table, only those oxides have been selected for purposes of comparison, which are, in any given family, common to *all of the members of that family*, or, in cases where the oxides themselves* are not known, their existence has been considered as theoretically possible because some derivatives of the missing oxides have been described. In any given family, any one of the oxides given on the above table in the vertical column belonging to that family, may be termed the *typical oxide* of that group.

By a skillful combination of the connections which have been emphasized in the last chapter, Mendelejeff was able to predict the existence of a number of elements, unknown at the time of his discovery of the periodic system; for the purpose of illustrating the method adopted by that investigator, one example will be given here.

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* For instance, the oxide Mn_2O_7 does not exist, but a salt derived from that oxide as an anhydride, $KMnO_4$, potassium permanganate, does exist, the same is true of the oxides I_2O_7 and Br_2O_7, the acids derived from these, and the salts of these acids are known, while the oxides themselves are unknown.

No element fitting into the fourth series, group three, was known, yet, were such a one to be discovered, it should, in its properties, be related to aluminium in the same way as calcium is to magnesium or as titanium is to silicon. Its atomic weight should be about 44, inasmuch as it would follow K, (39), Ca (40) and be followed by Ti (48) and V (51). In predicting the properties of this element Mendelejeff reasoned that it would be as much more metallic than aluminium as calcium is than magnesium, or as titanium is than silicon. This unknown element Mendelejeff called ekaboron, with a symbol Eb, and for the purposes of comparison the predicted properties of ekaboron and the real properties of scandium, the element which was subsequently discovered, are placed side by side:*

EKABORON.	SCANDIUM.
Atomic weight about 44.	Atomic weight, 44.
Oxide, $Eb_2 O_3$, soluble in acids, analogous to $Al_2 O_3$, but more basic, insoluble in alkalis.	Oxide, $Sc_2 O_3$, soluble in strong acids, analogous to $Al_2 O_3$, but decidedly more basic, insoluble in alkalis.
Salts of Eb, colorless, yield gelatinous precipitates, with Na OH, $Na_2 Co_3$.	Salts of Sc are colorless and yield gelatinous precipitates with Na OH, $Na_2 CO_3$.
Sulphate, $Eb_2 (SO_4)_3$, will form a double salt with $K_2 SO_4$, which will not be isomorphous with the alums.	Sulphate, $Sc_2 (SO_4)_3$, will form a double salt with $K_2 SO_4$, which is not isomorphous with the alums.

It seems scarcely necessary to enter into a more detailed description of the periodic system at this place; the elements, which have already been considered, have been discussed in their relation to the natural groups of which they are members, so that their individual connections have been sufficiently pointed out; those which are to follow will be described in the order given by the periodic system, while attention will be called to the character of the various families at the proper place. It does not fall within the scope of this work to give a detailed description of each individual metal, as has been done with the not metals, for that ground is very abundantly covered by the large number of works on qualitative analysis, which discuss many of the chemical reactions peculiar to the metals because the latter are mainly interesting from an analytical standpoint, and, moreover, much of the chemistry of the salts of the metals is merely a repetion of what has already been taken up.

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*See Pattison Muir, Principles of Chemistry, p. 201.

CHAPTER LII.

THE ALKALI METALS.

*Lithium, symbol **Li**, atomic weight, 7.02.*
*Sodium, symbol **Na**, atomic meight, 23.05.*
*Potassium, symbol **K**, atomic weight, 39.11.*
*Rubidium, symbol **Rb**, atomic weight, 85.5.*
*Caesium, symbol **Cs**, atomic weight, 139.2.*

The alkali metals are the chemical opposites of the halogenes, the latter are the most negative (not metallic) elements with which we are acquainted, while the former are the most positive. Just as the not metalic properties diminished from fluorine to iodine in the halogene group, so the metallic properties of the alkalis increase with increasing atomic weight, and these changes can, perhaps, best be studied by a comparison of the readiness with which the individual members of both families decompose water. This decomposition is of an exactly opposite character accordingly as the element in question is a member of the halogene or of the alkali group. As a reference to page 33 will recall, the halogenes decompose water, liberating oxygen, and they do this the more readily the *more negative* they are; on the other hand the alkalis decompose water, liberating *hydrogen*, and this reaction takes place the more readily the *more positive* the metal in question is. Fluorine, when brought in contact with water, instantly forms hydrofluoric acid, and sets free oxygen, even in the absence of light; chlorine does so only when the solution of that gas is placed in the sunlight; bromine enters into this reaction more slowly than chlorine, while iodine has no effect. In the case of the alkali metals, lithium decomposes water, forming lithium hydroxide and hydrogen, but the metal does so, quietly, without melting or without generating sufficient heat to cause the hydrogen to take fire; sodium attacks water energetically, the metal is heated to its melting point but the hydrogen which is being evolved does not burst into flame; potassium melts, while sufficient heat is developed to ignite the hydrogen, while both rubidium and caesium enter into the decomposition with explosive violence. Of course, the halogenes and the alkali metals unite with the greatest energy, the latter burn in an atmosphere of the former with a brilliant light, while most stable halides are produced.

The alkali metals are soft, malleable and ductile, and possess a brilliant metallic lustre. When exposed to the air they almost instantly become coated with a layer of oxide, the latter absorbs moisture and carbon dioxide, thereby changing into a mixture of the carbonate and hydroxide; as a consequence of these changes, pieces of the alkali metals which are in contact with the atmosphere soon become the center of a small pool of deliquescent hydroxide; because of this capacity for oxidation the metals are kept under some liquid hydrocarbon, such as petroleum.

Contrary to the rule observed with not metallic elements which form the opposite extremity of the periods, the metals in a given family at the beginning of the same show a diminution of their melting points, with an increase in their atomic weights; this change is evident from the following table:

Li,	specific gravity,	.589,	atomic volume,	11.9,	melting point,	180 °
Na,	" "	.972,	" "	23.7,	" "	95.6°
K,	" "	.865,	" "	45.2,	" "	62.5°
Rb,	" "	1.52,	" "	56.3,	" "	38.5°
Cs,	" "	1.88,	" "	74.0,	" "	26. °

The oxides of all the alkali metals are soluble in water, and when so dissolved produce the corresponding hydroxides. From this it follows that the former cannot be produced excepting by processes during which water is rigidly excluded. Each of the elements can be burned in oxygen, forming the corresponding oxide of the formula M_2O; these oxides greedily take up water, producing the hydroxides:

$$M_2O + H_2O = 2\,MOH,$$

while the latter, of course, can also be formed by dissolving the former in water. During this change from oxide to hydroxide and during the subsequent solution a large amount of heat is given off, for instance, in the case of Na_2O, the latter amounts to 550 K. The hydroxides are, without exception, soluble; this solubility increases with the metalic nature and hence with the atomic weights and volumes of the alkali metals, the more positive the metal, therefore, the more soluble the hydroxide; indeed, the hydroxides of the alkali metals alone are very readily soluble.* If we examine the next family to the right of the alkalis in the periodic system, we will discover that the hydroxides of the two members with the smallest atomic weights (beryllium and magnesium) are insoluble † while those of calcium, strontium and barium, although in no case as readily soluble as the hydroxides of the alkali metals, have their solubility *increased* with *increasing* atomic weight, so that the same rule, holding good with the alkali metals, appertains to this family also. With the families mentioned (the alkalis and the alkaline earths) the list of soluble hydroxides of the metals is practically exhausted, for by far the greater number of hydroxides of the purely metalic elements is insoluble in pure water.

The hydroxides of the alkali metals (the caustic alkalis) can be prepared by the action of the respective metals on water.

$$M + HOH = MOH + H,$$

or by covering slaked lime with a solution of an alkaline carbonate, allowing the mixture to stand and then filtering, when the following reaction has taken place:

$$\underset{\text{Soluble.}}{M_2CO_3} + \underset{\text{Soluble.}}{Ca(OH)_2} = \underset{\text{Insoluble.}}{CaCO_3} + \underset{\text{Soluble.}}{2MOH},$$

The filtered liquid is evaporated, at first in porcelain and finally in iron or silver dishes.‡ All of the alkaline hydroxides can be fused without decomposing into the corresponding oxide and water, and the solution of any one of them absorbs carbon dioxide when exposed to the air, so that, if it is to be kept for any length of time, it must be placed in closed flasks. The solutions are strongly alkaline in taste and in reaction toward litmus, and neutralize salts with the greatest readiness.

The phenomena attending the neutralization of an acid by a base are of such importance that a brief discussion of their nature is necessary. If, to use potassium hydroxide as an example, that base

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[*] The hydroxide of lithium alone, in the alkali family, is not soluble with great readiness.

[†] That of magnesium is very nearly insoluble.

[‡] Platinum vessels must not be heated with concentrated solutions of alkaline hydroxides, for they are readily attacked by caustic alkalis.

is brought in contact with hydrochloric acid, the following change, as expressed by our chemical equations, takes place:

$$KOH + HCl = KCl + H_2O.$$

Of the two systems, $KOH + HCl$ and $KCl + H_2O$, the former is in unstable equilibrium, the two systems correspond to two different quantities of energy, so that when the former is converted into the latter, energy is conducted away in the form of heat. The sum of the energy thus conducted away and of that remaining in the system $KCl + H_2O$ must be equal to that originally contained in $KOH + HCl$. We are also acquainted with chemical reactions in which energy must be conducted to a system in order to change it into a second one. The former class of reactions are exothermic, the latter are endothermic (page 11). In how many portions the energy may be communicated has evidently no effect on the final value. In the reaction cited above the following changes take place:

$$KOH + HCl = KCl + H_2O - (K, OH + H, Cl),^*$$

that is, there is an expenditure of energy sufficient to decompose KOH into $K + OH$ and HCl into $H + Cl$ necessary before the rearrangement into $KCl + H_2O$ takes place. In the entire reaction, however, energy passes off in the form of heat, and the amount of the latter is evidently independent of the intermediate changes. This may be expressed in the following terms: "The heat of formation of $KCl + H_2O$ is greater than that of $K, OH + H, Cl$." As we may disregard the intermediary changes, we can express the result as follows:

$$KOH\,aq + HCl\,aq = KCl\,aq + H_2O + aq + 137\ K,$$

the symbol aq. signifying that the constituents are dissolved in a quantity of water so large that the addition of any more of the reagents will not affect the thermal value, or, as the formation of water takes place in all neutralizations of acids with bases, and as its mixture with the salt solution can produce no thermal effect, we can write the equation:

$$KOH\,aq + HCl\,aq = KCl\,aq + 137\ K.$$

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* See Ostwald, Outlines of General Chemistry, page 368.

Now, it has been shown that different acids, as well as different bases, evolve different amounts of heat when neutralized, but *the difference between the amounts of heat given off by any two bases when neutralized by a series of acids or between any two acids when neutralized by a series of bases is always the same.* The strong monobasic acids (hydrochloric acid, hydrobromic acid, hydroiodic acid, nitric acid, chloric acid, bromic acid, perchloric acid, iodic acid) all give off very nearly the same amount of heat when neutralized by an equimolecular quantity of caustic soda; this amount is very nearly 139 K. Among dibasic acids, on the contrary, a different behavior is observed; although some, like the monobasic acids, liberate 139 K for each equivalent;* others, on the other hand, liberate more. For instance, if increasing quantities of sulphuric acid are added to a weight in grams of sodium hydroxide equivalent to one combining weight, an evolution of heat takes place until sufficient acid has been added to form the secondary sulphate, $Na_2\,S\,O_4$. This amounts to 157 K for one gram equivalent weight and 314 K for one gram formula weight of sulphuric acid. If sulphuric be further added an *absorption* of heat takes place until a limit of —33 K is reached. This absorption takes place during the formation of the primary sulphate (see page 149), so that we here observe the phenomenon of a reaction spontaneously inaugurated without the evolution of heat. The hydroxides of the alkali metals and of the alkaline earths form a group of bases which act similarly to the monobasic acids; when neutralized with hydrochloric acid they give off, for each equivalent weight in grams, about 139 K. Other hydroxides, like aluminium and ferric hydroxides, have much smaller heats of neutralization. The fact that so much heat is evolved when acids are brought in contact with bases explains why the reactions of neutralization take place so readily, and why the salts formed are so often among the most stable chemical bodies. Of course, some very weak acids are able only to partially neutralize bases and very weak bases to partially neutralize acids. The heats of neutralization in these cases will be small and the salts easily decomposed by the addition of water or of acids, or even by slight warming. Such examples have been encountered in the study of the chlorides of bismuth and antimony and in the study of hydrocyanic acid.*

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* By equivalent is meant one-half the formula weight, or that proportion by weight of the acid which would contain one part by weight of hydrogen.

When we use the expressions "strong" and "weak" bases it, however, becomes as necessary to define the meaning of those terms as it was when we used similar designations in regard to acids (see page 139). But little work, as compared with that done in the study of acids, has been accomplished in regard to the affinity of bases, yet we can place the ratio between the strengths of two bases as being given by the relative rapidity with which the two are able to decompose a salt of a third, not very pronouncedly metallic, substance.† Experiments in this direction have shown that the hydroxides of the alkali metals all act about equally in this respect, the alkaline earths are but little behind the alkalis, while ammonia develops a very slow action.

Our previous chemical study has shown that chemical changes depend upon the quantity of heat which is produced or absorbed during the various reactions and that they also depend greatly upon the temperature and other external conditions under which they take place. Now it is also a matter of common experience that the mass of the active chemical reagents has exactly the same influence as the temperature in such a way that an *increase* of the mass‡ may bring about the same effect as a *diminution* of temperature, and a diminution of the mass has the same effect as an increase of temperature. This relationship is made clear in reactions in which dissociation takes place, so, for instance, if molecules of $N_2\ O_4$ are dissociated to form $N\ O_2$, the reunion of molecules of $N\ O_2$ to form $N_2\ O_4$ will take place the more frequently in the unit of time the more often contact between the molecules takes place, but this contact will take the oftener the greater the density of the gas, *i. e.*, the smaller the space which a given quantity has at its disposal, the density of a gas increases with the pressure upon it, so that the active mass in the unit volume becomes greater. It follows that the amount of $N\ O_2$ found is *smaller* the greater the density, but it is also true that the amount of $N\ O_2$ will be *smaller* the lower the temperature. As a result of this and many similar investigations the law has become well established that the amount of chemical action which a substance can exert in any case is *proportional to the active mass of that substance* which is present in the unit volume. We make a daily empirical use of this law by using, for instance, concentrated acids to dissolve certain substances in preference to dilute ones. Let us suppose two substances, A B and C D to be in solution, and let us suppose that A B acts on C D to produce two new substances, A D and B C. At the first instant of the reaction the substances in solution can be expressed by the following:

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* See pages 243, 250, 285.

† Such a substance is methylacetate, $C\ H_3\ C\ O\ O\ C\ H_3$. In this substance the mono valent radicle *methyl* (page 266) takes the part of a metal.

‡ *I. e.*, of the quantity of reagent contained in the unit volume.

$$\frac{\text{A B}\quad\text{C D}}{\text{A D}\quad\text{B C.}}$$

These changes will go on until a point is reached in which A D and B C will be present in such mass that A D and B C, reacting on each other, will reproduce exactly as many molecules of A B and C D as A B and C D will produce of A D and B C. The solution is then in a state of equilibrium, which can be disturbed, however, by increasing the mass of one or the other of the constituents. Let us suppose, however, that A D, which is produced, is either insoluble or volatile, it is then removed from the solution as fast as it is formed, and let us further suppose that B C can have no effect on the insoluble or volatile substance produced. A familiar example of such a change would be the action of silver nitrate on hydrochloric acid, by which means silver chloride, which is insoluble, and nitric acid are produced:

$$\mathrm{Ag\,N\,O_3 + H\,Cl = Ag\,Cl + H\,N\,O_3.}$$

In such a case then, as the silver chloride is removed from the solution as fast as it is produced, no equilibrium can result until the entire mass of silver nitrate has been converted into silver chloride. The same would be true if the substance produced were a gas, and as a consequence would as certainly be removed as if it were an insoluble solid. These reactions, known as double decompositions, are among the most common which are to be considered in the chemistry of the metals. We have already encountered a number of them, an instance being the action of hydrogen sulphide on soluble salts of the heavy metals (see page 95) and the empiric rule has come about as the result of experience that a complete double decomposition takes place when an insoluble or volatile substance is produced.*

The sulphides of the alkali metals, owing to their resemblance to the oxides, naturally follow in the order of the discussion. These compounds are all quite soluble in water. They are formed, as a general rule, by reduction of the corresponding sulphates by heating with charcoal:

$$M_2SO_4 + 4C = M_2S + 4CO,$$

or by addition of hydrogen sulphide to a solution of the corresponding hydroxide, by which means the sulphhydrate is produced:

$$MOH + H_2S = MSH + H_2O.$$

An addition of an equal amount of hydroxide to the sulphydrate then produces the sulphide:

$$MSH + MOH = M_2S + H_2O.$$

(In this case H_2S acts like a dibasic acid; see page 137.)

The solutions of alkaline sulphides are able to dissolve sulphur to form so-called polysulphides (see page 151, foot note). In the cases of sodium and potassium, polysulphides having the following formulæ have been isolated:

Na_2S_2, K_2S_2,
Na_2S_3, K_2S_3,
Na_2S_4, K_2S_4,
Na_2S_5, K_2S_5.

All of these, on addition of acids, form the corresponding salt, hydrogen sulphide and sulphur, for instance:

$$K_2S_5 + 2HCl = 2KCl + H_2S + 4S.$$

When exposed to the air they are oxidized, forming salts of dithionic acid, while sulphur is liberated:

$$K_2S_2 + 3O = K_2S_2O_3$$
$$K_2S_3 + 3O = K_2S_2O_3 + S$$
$$K_2S_4 + 3O = K_2S_2O_3 + 2S$$
$$K_2S_5 + 3O = K_2S_2O_3 + 3S.$$

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* The laws of mass action have of late been greatly developed by a number of prominent chemists; their discussion is however out of place in an elementary text-book. For more detailed information the pupil can refer to Ostwald's Outlines of General Chemistry, Walker's translation.

The formulæ of these sulphides can perhaps be best explained on the supposition that they are salts of thio or sulpho acids, so that the action of sulphur on the monosulphides would be analogous to that of oxygen on the same substances. For example, the sulphide of potassium would be oxidized to the sulphate:

$$K_2 S + 4 O = K_2 S O_4,$$

while the sulphide would be sulphurized to the pentasulphide:

$$K_2 S + 4 S = K_2 S_5.$$

According to this theory the pentasulphide would be the potassium salt of dithio-disulpho sulphuric acid, or:

$$S\begin{cases} S\,K \\ S \\ S \\ S\,K. \end{cases}$$

This theory is, however, sustained only by the fact that the sulphides of the alkalis can take up no more than four atoms of sulphur. The acids corresponding to these sulphides have never been isolated.

The sulphhydrates of the alkali metals, corresponding to the hydroxides in formula, are soluble in water and are produced by the action of hydrogen sulphide on the hydroxides:

$$K O H + H_2 S = K S H + H_2 O.$$

Both the sulphides and sulphhydrates are bases; with acids they form salts and *hydrogen sulphide* (the oxides and hydroxides form salts and *water*; see page 92).

$$\begin{aligned} K_2 O + 2 H Cl &= 2 K Cl + H_2 O \\ K_2 S + 2 H Cl &= 2 K Cl + H_2 S \\ K O H + H Cl &= K Cl + H_2 O \\ K S H + H Cl &= K Cl + H_2 S. \end{aligned}$$

The halogene derivatives of the alkalis are extremely stable and are throughout soluble in water. Of these compounds, the most common in occurrence are the chlorides, of which sodium chloride is by far the most often met with. Sodium chloride, or common salt, occurs in extensive beds in rocks of various ages, associated with gypsum, calcite, clay and sandstone. It frequently occurs in solution in salt springs and is always found in the sea, of which it forms

2.5 per cent. The salt of commerce is often obtained by evaporating sea water in lagoons by means of the heat of the sun, as is done in France. Lime, gypsum and ferric hydrate separate at first, afterward the salt begins to crystallize and can be raked out; at last there is left a mother liquor which contains sodium chloride, magnesium chloride, potassium chloride and magnesium sulphate. In many cases, where the brine obtained from salt springs is evaporated, the mother liquors contain the *bromides* and iodides of the alkalis. The simple halides of the alkali metals crystallize in the regular system, most frequently in cubes. As we have seen (page 325) the halides of the alkali metals have a tendency to crystallize with other halides in the form of double salts in which the alkaline halide presumably plays the part of the base. A number of these double halides occur as natural minerals. Among the most important of them is cryolite, $Al\ F_3$, $3\ Na\ F$ (see page 321). None of the bromides or iodides of the alkalis occur as crystalline mineral individuals.

As would be expected, the heat of formation of the alkaline halides increases with the increasing metallic nature of the alkaline metal forming such a halide. This relationship is readily seen from the following table:

HEAT OF FORMATION OF THE CHLORIDES.

Li Cl, 938 K.
Na Cl, 976 K,
K Cl, 1043 K.

A distinctive feature of the chemistry of the alkali metals lies in the fact that the salts of these metals are almost without exception soluble in water; they can be produced by neutralizing the hydroxide solutions with the various acids.

The carbonates of the alkalis are soluble in water, differing in this way from those of the alkaline earths, however, being the carbonates of the most positive metals, they are not decomposed by heat, as are the same salts of all other elements; the carbonate of the least metallic element of the alkali family (lithium) is also the least soluble in water; the solubility of the carbonates, as we pass from member to member in this group, increases with the increase in the metallic character, and hence of the atomic weight of the alkali metal producing the salt. The most important carbonates are those of sodium and of potassium and, as sodium carbonate (common soda) is of great commercial importance, it is advisable to enter into a brief description of the process of its manufacture.

Sodium carbonate occurs in some mineral waters (Karlsbad) and as a remainder after evaporating the water of alkaline lakes, it is further a consituent of the ashes of sea-plants,* and it was from these latter that the soda of commerce was made up to the end of last century. During the period of the French Revolution a large reward was offered for the discovery of a process by means of which sodium carbonate could be prepared from the chloride, as the latter substance was a product which was both cheap and easily purified. Nicholas LeBlanc,† owing to this inducement, discovered a process which has been used with but little modification up to the present day. The chemical changes upon which this method depends are as follows:

Sodium chloride is treated with sulphuric acid, when hydrochloric acid and primary sodium sulphate are formed:

$$\mathrm{Na\,Cl + H_2\,SO_4 = Na\,H\,S\,O_4 + HCl.}$$

The primary sulphate is then heated with sodium chloride, producing hydrochloric acid and the secondary sulphate:

$$\mathrm{Na\,Cl + Na\,H\,S\,O_4 = Na_2\,S\,O_4 + HCl.}$$

The hydrochloric acid which passes off is absorbed by water and is used as ordinary commercial hydrochloric acid.

The sodium sulphate is next converted into crude soda by heating with anthracite coal and chalk (calcium carbonate), the temperature reaching 1000°. Despite the extended attention given to the soda manufacture in the last few years, the chemical processes taking place have not been definitely settled, yet the following are most frequently accepted as nearly correct:—Sodium sulphate first is reduced to sodium sulphide by charcoal:

$$\mathrm{Na_2\,S\,O_4 + 2\,C = Na_2\,S + 2\,C\,O_2;}$$

and the sodium sulphide, together with chalk, then changes to sodium carbonate and calcium sulphide,

$$\mathrm{Na_2S + Ca\,C\,O_3 = Na_2\,C\,O_3 + Ca\,S.}$$

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* The ashes of land plants consist mainly of potassium carbonate.

† Physician to the Duc d' Orleans.

The crude soda is extracted with water and the liquors are evaporated, when tolerably pure sodium carbonate crystallizes. This, when slowly crystallized from water, separates with ten molecules of that substance and forms crystals of commercial soda, $Na_2CO_3 + 10H_2O$. The latter effloresce when in contact with the air, losing 9 molecules of water and changing into a powder, which has the composition $Na_2CO_3 + H_2O$.

A modern process, known as the ammonia-soda process, has of late succeeded to a large extent in taking the place of the older method. This late improvement depends on the fact that primary sodium carbonate is soluble with difficulty. Ammonia solution, saturated with an excess of carbon doxide, contains primary ammonium carbonate $(NH_4)HCO_3$; when this is added to a solution of common salt the following change takes place:

$$(NH_4)HCO_3 + NaCl = NaHCO_3 + NH_4Cl;$$

the primary sodium carbonate (sodium bicarbonate) separates as a crystalline powder, and the latter, when heated, gives off water and carbon dioxide, leaving the secondary carbonate (see page 280)

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The nitrates of sodium and of potassium are of importance in the manufacture of gun powder. Sodium nitrate is found in the northern part of Chili,* where it occurs in extensive deposits, accompanied by sodium chloride and other salts the presence of which seem to indicate that the formation of the nitrate is due to the decay of marine plants, the occurrence of these deposits in this place being one of the proofs of the theory that this portion of South America was at one time submerged. Sodium nitrate is purified by washing with water and recrystallization; the mother liquors which are left contain considerable quantities of the iodides and are used in the manufacture of iodine. Unfortunately, sodium nitrate, because it is hygroscopic, cannot be used in the preparation of gun powder, so that, preliminary to the production of that explosive, the nitrate of sodium must be converted into nitrate of potassium; this is accomplished by treating a saturated solution of sodium nitrate, at boiling heat, with a solution of potassium chloride, when a double decomposition, accompanied by the formation of the less soluble chloride of sodium, takes place:

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* Province of Tarapaca, the nitrate is called Chili saltpeter.

$$NaNO_3 + KCl = NaCl + KNO_3.$$

The solution of potassium nitrate is filtered and allowed to crystallize. Potassium nitrate occurs as a mineral deposit in many places where nitrogenous organic matter is decaying in the presence of potash (see page 195), localities in which this natural production of potassium nitrate assumes commercial importance are found in Spain, Egypt, Peru, and especially India, from which latter country potassium nitrate is exported in considerable quantities.

The use of potassium nitrate in the manufacture of gun powder depends on the oxidizing powers of that substance. When potassium nitrate is mixed with charcoal and ignited, the following reaction takes place.

$$2KNO_3 + 3C = CO_2 + CO + K_2CO_3 + 2N,$$

the carbon dioxide, which is left in combination as potassium carbonate, can be further liberated by the previous addition of sulphur:

$$2KNO_3 + 3C + S = K_2S + 3CO_2 + 2N.$$

The formation of such a large amount of gaseous material from the small volume of solid causes the explosion. The reaction given is, however, only approximately correct, for other changes, not definitely understood, also take place.

The other salts of the alkalis have been sufficiently mentioned in the course of the chapters in which the various acids have been discussed. The following table will make the formulæ and solubility of some of the salts most apparent.

ALKALI METALS.

OXIDES, M_2O, converted to the hydroxides by addition of water.

HYDROXIDES, MOH, soluble in water, least soluble is $LiOH$, solubility increases with increasing atomic weight of the alkali metal.

SULPHIDES, M_2S, soluble, probably converted into $MSH + MOH$ by addition of water.

SULPHHYDRATES, MSH, soluble in water; $MOH + H_2S = MSH + H_2O$.

CARBONATES, M_2CO_3 and $MHCO_3$, soluble in water, least soluble is Li_2CO_3, solubility increases with increasing atomic weight.

NITRATES, MNO_3, soluble in water, change to *nitrites* and oxygen when heated. (See page 154.)

SULPHATES, M_2SO_4 and $MHSO_4$. Soluble in water.

PHOSPHATES, $M H_2 P O_4$, $M_2 H P O_4$. $M_3 P O_4$. tertiary phosphates change to secondary phosphate and hydroxide of alkali metals on addition of water. (See page 221.)

SILICATES, $M_2 Si O_3$, soluble in water.

POTASSIUM PERCHLORATE, $K Cl O_4$, potassium fluosilicate, $K_2 Si F_6$ are soluble with difficulty and hence are precipitated from solutions of potassium salts by addition of the corresponding acids, sodium pyroantimonate, $Na_2 H_2 Sb_2 O_7$ insoluble in cold water.

The salts of ammonium correspond entirely to the salts of potassium, and hence are frequently discussed in connection with the alkali metals. Their nature has been sufficiently explained on page 182 and *sub.*

The readiest means for the detection of the various alkali metals is by means of the spectroscope, indeed, caesium and rubidium were not known to exist until the examination by the spectroscope of the residues left by evaporation of certain mineral waters revealed their presence. The principle upon which the use of the spectroscope depends is as follows:—Light which contains waves of only one wave length is monochromatic (homogenous). When a ray of such light, passing through the air, comes in contact with a transparent medium of greater density it is refracted toward a line normal to the surface of the latter, and the smaller the wave-length the greater is the refraction; for each wave-length there is a corresponding index of refraction, provided the media through which each kind of light passes remain the same. If a ray of light contains waves of various lengths, then each kind of wave will be refracted according to its refractive index, so that the whole will be separated into as many monochromatic rays as it contained different wave-lengths. Such a ray of light, falling from a narrow slit upon a prism the edge of which is parallel to the slit, produces a series of parallel images of the opening, and if the light consists of all of the colors between two determined extremes, the image obtained appears a continuous spectrum produced by a number of different colored images of the slit, which merge the one into the other. Light which is emitted by the sun or by white hot bodies, contains an infinite number of different waves and is termed white, when passed through the prism it gives a spectrum containing all the colors of the rainbow, beginning with red and passing through the various modifications of color, (orange, yellow, green, blue), to violet at the opposite extremity. The spectroscope, (Fig. 49) consists of a telescope (A) which throws parallel rays of light admitted through a small slit at (S) upon a prism (P), the spectrum formed is observed by the telescope at B, which is so focussed as to give a sharp image of the same, at the same time a mirrored image of a millimeter scale photographed and placed in C, is so reflected as to be visible above the spectrum when the observer glances through B.

The spectrum of a white hot solid when so observed is continuous, but this is not the case with glowing gases. These, when examined by the spectroscope, show a number of bright, colored lines upon a black or nearly black background. The *colors and relative position* of the lines are definite ones for each individual glowing gas, and are always different for gases of differing chemical composition. The reason for the appearance of these lines is that the glowing gases emit light only of certain determined wave-lengths, the varieties, and hence the colors, of which are generally few in number, as a consequence, light of each wave-length being refracted according to its index of refraction, appears in a different place on the spectrum as a sharp line of the color belonging to that particular wave-length.

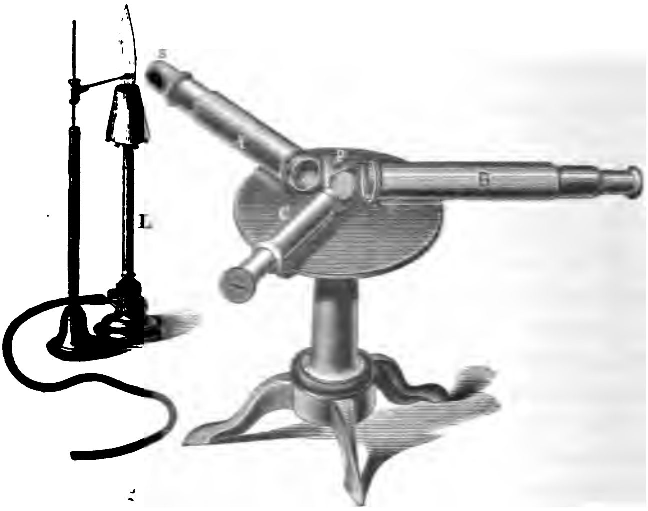

FIGURE 49.

The flame of a Bunsen burner is not luminous, but if a platinum wire is placed in it, the latter becomes heated and emits a white light. If, now, the wire is coiled as in Fig. 50, and is, after moistening with a little hydrochloric acid, dipped into a little sodium chloride, the adhering salt, when brought into the flame, will be vaporize and will emit a pure yellow light; in the same way, potassium will be violet;* lithium or strontium red; copper, barium or thallium, green; zinc, blue, etc.† If the yellow sodium light is observed by means of a spectroscope, a bright yellow line in a dark background is seen to appear. The position of this yellow line corresponds to the position occupied by yellow in the continuous spectrum. Lithium will show a red line and a less marked yellow one, potassium a red line and a blue one. In fact, each individual metal displays characteristic lines in definite parts of the spectrum, while the lines of no two metals correspond exactly. In order, then, to discover the presence of any metal or metals in a mixture, it is only necessary to place volatile compounds of those elements in the not-luminous flame and then to observe the spectrum so produced. The minutest traces can be detected in this way.

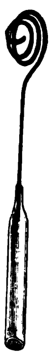
FIGURE 50.

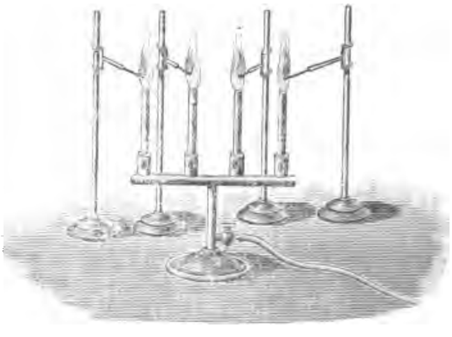
FIGURE 51.

If a not-luminous flame is placed in front of a luminous background which emits a white light, and if then some sodium salt is volatilized in this not-luminous flame, the spectroscope will show a continuous spectrum, due to the white light, with this difference, however, that in the place where the yellow band of light belonging to the sodium spectrum usually occurs, there is now seen a black band, this phenomenon being due to the fact that when a ray of white light containing all colors is passed through a glowing gas which emits light rays only of certain definite colors, this glowing gas is able to absorb from the white light the rays of exactly the same color which it itself emits. It follows that when white light is passed through the glowing vapor of a potassium compound there will appear on the continuous spectrum a dark line in the red and one in the blue; in the case of lithium, a dark line in the red and one in the yellow, etc. Such spectra are called absorption spectra. The spectra of the sun and of the fixed stars are not perfectly continuous, but are traversed by a series of fine, dark lines which have been proven to correspond exactly to the absorption spectra of the glowing vapors of elements with which we come in contact on the earth; the spectra of the sun and the fixed stars are therefore absorption spectra, caused by the white light of the glowing central mass passing through the surrounding chromosphere, which latter must contain a number of elements in the state of glowing vapors; and those elements are identical with the ones encountered on the earth.* By means of the spectroscope we have therefore been able, to a great extent, to analyze the composition of glowing gases which surround the sun and the fixed stars.

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* Best seen when the potassium flame is observed through a piece of blue glass When sodium is also present, the blue absorbs the yellow rays while permitting the violet to pass through.

† The contrasting colors of the various flames can be best observed by using a lamp with four or five burners (Fig. 51) and, after fixing platinum wires in the stands, as shown in the figure, bringing the entire number simultaneously into the lighted burners.

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*Some lines appear in the spectrum of the sun which do not correspond to those emitted by any known element.

CHAPTER LIII.

COPPER, SILVER AND GOLD.

Copper, Symbol Cu, atomic weight, 63.4;
Silver, Symbol Ag, atomic weight, 107.92:
Gold, Symbol Au, atomic weight, 197.3.

These three elements find their places at the beginning of the second section of the long periods and, because the second portion of the latter shows many points of resemblance to the first, we must expect copper, silver and gold to be in some respects like the alkali metals, of which family they form the secondary group (see page 351). Naturally, as copper, silver and gold are much nearer to the not-metallic end of the long periods than are the alkali metals, we must not, in the chemical behavior of the former, look for metallic properties by any means so pronounced as are encountered with the latter; this difference is manifested in marked degree by the fact that neither copper, silver nor gold decompose water; the resemblances between the elements of this group and the alkalis are confined chiefly to their univalence, by reason of which each element forms halogene derivatives having the formula MX, corresponding to those of the alkali metals, and to the isomorphism between the crystalline form of some of the compounds derived from these elements in their univalant condition and similar compounds of the alkalis (of the latter especially those of sodium); on the other hand, copper and gold differ very widely from the alkalis by being able to form higher oxides and salts derived from these; in the case of copper this higher oxide has the formula CuO, of gold, Au_2O_3. The oxides M_2O and the hydroxides and halides derived from these are therefore the typical compounds belonging to the entire family comprising the alkali metals as well as copper, silver and gold, but those members of this family which find their places *at the beginning of the secondary division of the long periods* are also able to form oxides in which the valence of the elements is *more than unity*. In the formation of the latter oxides the elements in question (Cu, Ag, Au), appear as connecting links between the elements of the eighth group (Fe, Co, Ni), and the second half of the long periods. Copper, silver and gold find their places as the minima and the beginning of the second portions of the curves of atomic volumes; they are therefore malleable, ductile, fusible, electropositive and good conductors of electricity.

Their chief physical constants are given in the following table:

	Atomic Weight.	Specific Gravity.	Atomic Volume.	Melting Point.
Copper.....	63.4	8.8	7.2	1050°
Silver......	107.92	10.5	10.2	950°
Gold.......	197.3	19.3	10.2	1030°

All of these elements are volatilized when heated in the flame of the oxyhydrogen blowpipe. They crystallize, as do the alkali metals, in forms belonging to the regular system.

The most important mineral forms in which these elements occur are given in the following table:

COPPER.—As native copper, Lake Superior region, Siberia, Chili, Australia; as chalcocite (cuprous sulphide) $Cu_2\ S$, in Cornwall, Siberia, Saxony, Lake Superior; as chalcopyrite (copper pyrites) $Cu\ Fe\ S_2$, similar localities to chalcocite; as cuprite, $Cu_2\ O$, in Lake Superior regions; as melaconite, $Cu\ O$, in Lake Superior regions.

Copper also frequently occurrs, combined with arsenic and antimony trisulphides, in the mineral tetrahedrite (grey copper ore, fahl ore) which has approximately the formula, $4\ (Cu_2,\ Ag_2,\ Fe,\ Zn,)\ S,\ Sb_2\ S_3$, or $4\ (Cu_2,\ Fe,\ Zn)\ S,\ As_2\ S_3$. As the formulæ will show, iron and zinc accompany copper in these ores, while silver is also frequently encountered therein.[*]

In addition to the above sulphur compounds, the basic carbonates of copper, malachite, $Cu_2\ (H\ O)_2\ C\ O_3$, and lazurite, $Cu_3\ (H\ O_2)\ (C\ O_3)_2$, are important minerals.

SILVER.—As native silver, in the United States, Mexico, Peru, Norway, Saxony, Bohemia, Siberia, etc.

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[*] In this mineral two atoms of copper replace one of zinc or of iron isomorphously. The possibility of this replacement is probably due to the fact that the size of the molecule prevents an undue infinence on the crystalline form by one or two atoms, nevertheless it serves admirably to illustrate the necessity of great caution in using the laws of isomorphism for the purpose of determining atomic weights (see page 343).

As argentite, $Ag_2 S$, isomorphous with chalcocite, $Cu_2 S$; silver sulphide also occurs in conjunction with lead sulphide and in numerous minerals in which it is combined with the sulphides of antimony, $Sb_2 S_3$, arsenic, $As_2 S_3$, and iron, $Fe_2 S_3$.

GOLD.—As native gold in quartz veins in conjunction with iron pyrites, chalcopyrite, galena and other sulphides. Gold particles also occur in the gravel or sand of rivers or valleys in auriferous regions or on the slopes of mountains or hills whose rocks contain in some part auriferous veins.

Compounds of gold are very infrequent as minerals. The telluride of gold and silver, $(Ag, Au)_2 Te$, is sometimes found.

METALLURGY OF COPPER.—The copper ores, the most valuable of which are the oxides and sulphides, are roasted; by this means the volatile compounds of arsenic and antimony are removed while the sulphides of iron, which are present, are easily converted into the oxides, the sulphur passing off as sulphur dioxide. If the material used in the preparation of copper should contain large quantities of quartz, the latter substance in melting will attack the ferric oxide in order to form the silicate of iron, which can be run off in the form of slag; if the ores used do not already contain silicon dioxide, the latter must be added as quartz or sand. The product obtained after the roasting is much richer in copper than the original ore and contains both cuprous and cupric oxides as well as the corresponding sulphides. This material is again roasted and the remaining iron separated as slag, while the oxides and sulphides of copper mutually reduce each other as follows:

$$Cu_2 S + 2\, Cu_2 O = 6\, Cu + S O_2$$
$$Cu_2 S + 2\, Cu O = 4\, Cu + S O_2.$$

It is frequently necessary to repeat the roasting process several times while adding the coal and sand. Finally, the fused copper is stirred with poles of green wood. Not infrequently the copper ores contain considerable quantities of silver, so that the separation of the latter becomes profitable. The processes used are, however, somewhat complicated and need not be entered into in this work.

SILVER.—Considerable quantities of silver are obtained from galena (Pb S, lead sulphide) and separated from the lead by the process of cupellation, a description of which was given on pages 309 and 310. The quantities of silver in the lead ore may so vary that at one time the silver is the chief product of the process, while at

Copper forms two oxides,* cuprous oxide, $Cu_2\ O$, and cupric oxide, $Cu\ O$. Cuprous oxide is found in nature as the mineral cuprite, occurring in octahedra or in cubes; in the laboratory the oxide can be produced by heating a mixture of copper and cupric oxide to a red heat:

$$Cu + Cu\ O = Cn_2 O.$$

A hydroxide corresponding to this oxide is unknown, however, when a solution of copper sulphate, mixed with glucose, is warmed with alkalis, a yellow precipitate which has the formula $4\ Cu_2 O + H_2 O$ is produced, this substance is not completely dehydrated until a temperature of 360° is reached. When exposed to the air it rapidly takes up oxygen, forming blue cupric hydroxide, $Cu(OH)_2$; cuprous oxide dissolves in ammonia to produce a colorless fluid which, however, soon absorbs oxygen from the atmosphere and assumes a deep blue color. Cuprous oxide is very easily decomposed by many oxy-acids, and for this reason very few cuprous salts are known; dilute nitric or sulphuric acids attack it, liberating metallic copper and producing the corresponding *cupric* salts:

$$Cu_2\ O + H_2\ S\ O_4 = Cu\ S\ O_4 + H_2\ O + Cu.$$

The most important cuprous salts are the cuprous halides.

Cuprous chloride, $Cu\ Cl$, is a white solid *which is with difficulty soluble in water.* In this respect it resembles the corresponding chloride of silver. Like the latter it is readily dissolved by ammonia, with which it forms a substance having the formula $N\ H_3\ Cu\ Cl$; the latter compound possibly consists of ammonium chloride, $N\ H_3\ H\ Cl$, with the difference that one atom of hydrogen has been replaced by copper, so that in the formation of this body cuprous chloride would act as does hydrochloric acid in ammonium chloride. Cuprous chloride is readily oxidized when exposed to the air.

Cuprous iodide is the only iodide of copper which exists. It is formed by adding the solution of an iodide to a copper sulphate solution; the cupric iodide, which we would expect to have formed, at once breaking down into cuprous iodide and iodine:

$$Cu\ S\ O_4 + 2\ K\ I = K_2\ S\ O_4 + Cu\ I + I.†$$

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* An oxide $Cu_4\ O$ has also been described.

† The iodine which is liberated can be removed by the addition of a reducing agent such as $S\ O_2$ (see page 136).

Cupric oxide, $Cu\,O$, is the most stable oxide of copper. It can readily be formed by heating copper in a current of air or of oxygen, or by decomposing cupric nitrate, $Cu\,(N\,O_3)_2$, (page 199, β). It is a black substance which readily loses oxygen when it is heated in a current of hydrogen (see page 37) or with charcoal:

$$Cu\,O + C = Cu + C\,O.$$

Cupric hydroxide, $Cu\,(O\,H)_2$, is formed, just as are the hydroxides of most metals, by precipitation from the solution of a copper salt upon the addition of a soluble hydroxide. It appears as a blue, flaky precipitate which readily loses water when it is warmed; it then turns black and forms cupric oxide. Ammonia water dissolves both the oxide and hydroxide; the solution has a deep blue color which can be observed even when only very little copper is present. Both cupric oxide and hydroxide are bases; they dissolve in acids to form stable cupric salts. The latter, when they contain water of crystallization, are generally blue or green.

Cupric chloride, $Cu\,Cl_2$, is formed by the action of chlorine on copper or by dissolving the oxide or hydroxide and then evaporating and drying at 100°; when anhydrous it is a brown powder; when crystallized from water it forms green crystals of the composition $Cu\,Cl_2 + 2\,H_2\,O$; it is readily soluble in water. The chloride forms double salts with the chlorides of the alkali metals. The bromide resembles the chloride in every respect.

Cupric sulphate, $Cu\,S\,O_4 + 5\,H_2\,O$ (blue vitriol), is formed by dissolving copper in sulphuric acid (page 133).* The commercial product is prepared by roasting copper sulphide in a current of air, extracting with water and recrystallizing. It forms large, blue crystals belonging to the triclinic system; it is readily soluble in water. When exposed to the air the crystals effloresce and lose two molecules of water of crystallization; at 100° two more molecules pass off, so that a salt of the composition $Cu\,S\,O_4 + H_2\,O$ is left; the latter is probably a secondary salt of the hydrated sulphuric acid having the formula $H_4\,S\,O_5$ and should therefore be written $Cu\,H_2\,S\,O_5$. At 230° the two hydroxyle groups present in this salt (see page 149) finally separate water, leaving a white powder having a composition expressed by the formula $Cu\,S\,O_4$; as soon as water is added to this, a blue solution containing $Cu\,S\,O_4 + 5\,H_2\,O$ is produced; the latter belongs to a class of sulphates known as the vitriols (see magnesium). Copper sulphate can unite with ammonia to form compounds in which molecules of ammonia take the place of molecules of water of crystallization,* for instance, salts having the composition $Cu\,S\,O_4 + 5\,N\,H_3$, $Cu\,S\,O_4 + 4\,N\,H_3 + H_2\,O$, $Cu\,S\,O_4 + 3\,N\,H_3 + 2\,H_2\,O$, etc., are capable of existence. These substances furnish examples of cases where *the compound of nitrogen and hydrogen plays the same role as the compound of oxygen and hydrogen* (see page 288). An adequate chemical explanation for the reason of the existence of salts with water of crystallization and of these ammonium compounds, provided we adhere to our present theories of valence, is as yet lacking.† A number of basic sulphates of copper have been described.

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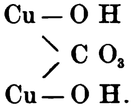
* In this reaction several secondary products (cuprous sulphide, $Cu_2\,S$, and compounds, $Cu_2\,S$, $Cu\,O$, and $Cu\,S$, $Cu\,O$) are produced.

Cupric nitrate, $Cu\,(N\,O_3)_2 + 3\,H_2\,O$, is formed by dissolving copper in nitric acid (see page 198) or by adding nitric acid to cupric oxide or hydroxide. The salt exists in blue, prismatic crystals which are soluble in water and which break down completely into cupric oxide and nitrogen peroxide when heated (see page 199).

Basic carbonates of copper.—The secondary normal carbonate, $Cu\,C\,O_3$, is unknown. A basic carbonate which has the same composition as the mineral lazurite is produced by adding the solution of a carbonate of an alkali metal to a solution of a copper salt. The carbonate is insoluble in water and has the composition $Cu\,(O\,H)_2\,Cu\,C\,O_3$ or:



Other basic carbonates (malachite, for example) occur in the form of minerals. All copper carbonates, when heated to 300°, lose car-

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[*] The same is true of cupric chloride, $Cu\,Cl_2 + 2\,H_2\,O$, for a substance of the composition $Cu\,Cl_2 + 2\,N\,H_3$ is known.

[†] The nitrogen atom in ammonia is unsaturated, as is proved by the easy formation of ammonium compounds. The resemblance between ammonia and water in these salts would lead us to suspect that the oxygen atom is also unsaturated in water. This conclusion is not very startling if we take into consideration the great resemblance between oxygen and sulphur, the latter element being able to take part in compounds in which its atoms are hexavalent.

bon dioxide and leave cupric oxide. The green coating of copper which has been exposed to moist air is due to the formation of a basic carbonate.

Sulphides of copper.—Copper forms two sulphides which, in formula, correspond to the oxides. *Cuprous sulphide,* $Cu_2 S$, occurs as the mineral chalcocite and is also most probably a constituent of chalcopyrite, for the latter substance is regarded as a sulpho-salt in which cuprous sulphide is the base and ferric sulphide the acidic anhydride:

$$Cu_2 S + Fe_2 S_3 = Cu_2 Fe_2 S_4.^*$$

Cuprous sulphide is a substance which is formed with remarkable readiness, for it can be produced by merely pressing copper and sulphur firmly together,† or by heating or even rubbing copper with a sufficient quantity of sulphur to form cuprous sulphide.

Cupric sulphide, Cu S, is produced by precipitating a slightly acid solution of a copper salt by means of hydrogen sulphide (see page 95). Cupric sulphide dissolves in hot hydrochloric acid, forming hydrogen sulphide and cuprous chloride. Nitric acid dissolves it, producing cupric nitrate, $Cu (N O_3)_2$, while the hydrogen sulphide, which is liberated, is oxidized to sulphur (see page 197). The precipitate is nearly black and when moist is readily oxidized to cupric sulphate when exposed to the air:

$$Cu S + 4 O = Cu S O_4.$$

When heated to 200° in a current of hydrogen it is changed into cuprous sulphide.

Compounds of silver.—Silver is univalent in nearly all of its compounds. Its most stable oxide is $Ag_2 O$, but oxides having the formula $Ag_4 O$‡ and Ag O are also known. The oxide $Ag_2 O$ is produced by adding a soluble hydroxide to a solution of a silver salt. It is a black precipitate which readily dissolves in an excess of ammonia (compare with cuprous oxide). When heated it readily breaks down into silver and oxygen.

Silver chloride, Ag Cl, one of the most characteristic silver salts, is insoluble in water and is therefore produced as a white precipitate when hydrochloric acid or the solution of a chloride is added to a solution of a silver salt:

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* One-half the formula weight of the above salt would lead to the usual formula of chalcopyrite, namely, $Cu Fe S_2$.

† This sulphurizing action reminds us forcibly of the oxidation of copper in the air.

‡ The existence of this oxide is doubtful; it is possibly a mixture of metallic silver and of $Ag_2 O$.

$$\begin{array}{ccccccc} \mathrm{Ag\,N\,O_3} & + & \mathrm{H\,Cl} & = & \mathrm{H\,N\,O_3} & + & \mathrm{Ag\,Cl}\text{[*]} \\ \mathrm{Ag\,N\,O_3} & + & \mathrm{Na\,Cl} & = & \mathrm{Na\,N\,O_3} & + & \mathrm{Ag\,Cl.} \\ \text{Soluble.} & & \text{Soluble.} & & \text{Soluble.} & & \text{Insoluble.} \end{array}$$

Owing to this insolubility the formation of silver chloride affords a ready means of detecting the presence of either silver or of a chloride in a solution. When silver chloride is exposed to the light it rapidly changes color, becoming violet at first; that color however soon becomes darker until the entire mass turns black. The same change also takes place with the equally insoluble bromide or iodide of silver, which latter salts can be formed by precipitation exactly as is the chloride. The chloride of silver is sometimes found as a mineral the name of which is cerargyrite. Silver chloride is very readily dissolved by an aqueous solution of ammonia; silver bromide is less soluble in that medium, while silver iodide is entirely insoluble. When heated with hydrochloric acid, both the bromide and iodide of silver are converted into the chloride, but, on the other hand, the chloride of silver changes into the bromide when treated with cold hydrobromic acid, and both the chloride and bromide are converted into the iodide when covered with cold hydroiodic acid and allowed to stand.[†]

One of chief uses of the silver halides is in the art of photography, their application depends on the fact that light effects such a change in these compounds as to cause the subsequent formation of a film of finely divided metallic silver upon those portions of a glass plate which have been covered with a thin layer of silver halide and which have been acted upon by the light, this film being produced when the silver halides are treated with certain reducing solutions;[‡] the unchanged silver halide is subsequently removed by solutions which have a solvent action on the unchanged salts but which leave metallic silver untouched. A solution of this nature is, for instance, one of sodium thiosulphate (hyposulphite) $Na_2\,S_2\,O_3$ (see page 150).[§]

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[*] See page 364.

[†] These changes afford an excellent example of the reversability of many chemical reactions when the conditions are changed.

[‡] So-called developers—ferrous sulphate, pyrogallic acid, hydrochinon, etc.

[§] The cause of the solution is the formation of the soluble double thiosulphate of silver and sodium, $Ag_2\,S_2\,O_3,\ Na_2\,S_2\,O_3$.

A plate covered with a thin layer of gelatine, containing some silver halide very evenly distributed throughout the mass, is exposed to the light in such a manner that a perfectly clear image of some object to be photographed is thrown upon it by means of a camera. The changes in the silver salt then take place according to the intensity of the light thrown upon the object. When the silver is finally deposited on the plate by means of the processes which have been outlined above, a perfectly clear image of the object to be photographed is left. The plate so produced is a "negative;" the photograph is prepared from this by covering paper with a sensitive film similar to that which was used on the negative and then exposing a piece of this, placed under the negative upon which the image has been fixed, to the action of the light; the picture is then produced in such a manner that, wherever a dark spôt appears on the negative, a light spot will be seen on the photograph. The latter is subsequently developed and fixed by a process similar to that used in the preparation of the negative.

The chemical action of light on the silver halides is not as yet definitely understood. The chemical changes which are useful in the art of photography are not, however, by any means the only ones which we encounter which are caused by light. Hydrogen and chlorine, it will be remembered, were entirely without action on each other when in the dark, but united with the greatest readiness in the sunlight; the compounds of carbon and hydrogen (see page 266) are substituted by halogenes when placed in the light but are not attacked in the dark, while many vegetable dyes bleach with the greatest rapidity when under the influence of the sunlight. The action of light in bringing about chemical changes is much like that of heat; yet not all light rays are capable of causing such changes; that power is reserved only for those waves of definite length which are found in the portion of the spectrum occupied by blue and violet and in the dark regions a short distance beyond the latter. The light rays which are capable of causing chemical reactions are designated as actinic rays.

Silver nitrate, $Ag\,N\,O_3$, is formed by dissolving silver or silver oxide in nitric acid; it is soluble in water and is separated from its solution by evaporating.* The salt crystallizes in plates belonging to the rhombic system and can be fused at 224° without changing its composition; the fused salt is cast into sticks and is popularly termed "lunar caustic." Silver nitrate is not changed when exposed to the light, unless some organic substances (dust, etc.) are brought in contact with it; it then turns black, owing to reduction and formation of metallic silver.* Dry silver nitrate absorbs ammonia quite readily; the same is true of the dry chloride. The latter substance forms a compound, $2\ Ag\ Cl + 3\ N\ H_3$,† which loses ammonia when heated. This power of absorbing ammonia is one of the most marked resemblances between silver and copper salts.

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*Silver nitrate in a pure form can be precipitated from its concentrated aqueous solutions by the addition of concentrated nitric acid, in which substance it is insoluble or nearly insoluble.

Sulphide of silver, $Ag_2\ S$, is formed by fusing sulphur and silver together, or by precipitation from the solution of a soluble silver salt by means of hydrogen sulphide; the natural mineral argentite, $Ag_2\ S$, has a metallic appearance much like that of lead; the precipitated sulphide is black. The compound is readily decomposed by heating with lead or iron; by this process the sulphides of the latter metals and free silver are produced. The blackening of silver when exposed to the air is brought about by the action of hydrogen sulphide; the minute traces of that gas which are present in the atmosphere attack the silver and form silver sulphide.

Many other salts of silver have been investigated. Many of these display a tendency to form double salts with other silver compounds or with the salts of the alkali metals. For their description a larger work must be consulted.

Compounds of Gold.—Gold forms three oxides, aurous oxide, $Au_2\ O$, aurous-auric oxide, $Au_4\ O_4$, and auric oxide, $Au_2\ O_3$. The first of these is produced with great difficulty and is of no great importance excepting as an illustration of the resemblance between the compounds of gold, silver and copper. The last one, $Au_2\ O_3$ is both a base and an acid. The hydroxide, $Au\ (O\ H)_3$ loses water when allowed to stand, changing to a metahydroxide of the formula $Au\ O\ (O\ H)$; the latter changes to auric oxide at 150°; at 220° auric oxide decomposes completely into gold and oxygen. The greatest difficulty which is encountered in the study of gold compounds lies in the readiness with which they break down and separate metallic gold. Auric oxide is readily dissolved by potassium or sodium hydroxide; the salts produced are derived from meta-auric hydroxide, $Au\ O_2\ H$, so that they have the formula $M\ Au\ O_2$; in this respect auric oxide resembles the oxide of aluminium (see pages 325 and 326).

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* Silver nitrate, when in contact with the skin, produces a black stain.

† Other compounds, $Ag\ Cl + 3\ N\ H_3$ and $Ag\ Cl + 2\ N\ H_3$, have also been described.

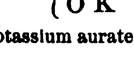
Chlorides of gold.—Three chlorides of gold, corresponding to the oxides, are known. They are $Au\ Cl$, aurous chloride; $Au_2\ Cl_4$, aurous-auric chloride, and $Au\ Cl_3$, auric chloride. The first of these, $Au\ Cl$, is insoluble in water. When the substance is covered with water and allowed to stand, it breaks down into auric chloride (which is soluble) and metallic gold:

$$3\ Au\ Cl = Au\ Cl_3 + 2\ Au;$$

but, on the other hand, a solution of auric chloride, when evaporated, breaks down into aurous chloride and free chlorine.

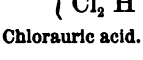
Auric chloride.—Gold is dissolved by aqua regia; the substance contained in solution is auric chloride, but the latter cannot be isolated by evaporation, because, as was just mentioned, it decomposes into aurous chloride and chlorine. Gold, when finely divided, and treated with dry chlorine, forms aurous-auric chloride, $Au_2\ Cl_4$, at a temperature of 180°; the latter, when heated to 220°, breaks down into gold and auric chloride; the auric chloride sublimes and collects on the cooler surfaces. Chlorine does not attack gold at 300°. A solution of auric chloride can also be prepared by allowing aurous chloride to stand covered with water (see above); when this solution is carefully evaporated, crystals having the composition $Au\ Cl_3 + 2\ H_2\ O$ are formed.

Chlorauric acid.—When a solution of gold in aqua regia, to which concentrated hydrochloric acid has been added, is evaporated, crystals of an acid, $H\ Au\ Cl_4 + 4\ H_2\ O$, separate. This compound is another one of the class of substances of which fluosilicic and fluoboric acids (pages 291, 318) and the double salts of aluminium are examples (see page 325), two chlorine atoms taking the place of one oxygen atom; the parallelism becomes clear when we compare the formula of potassium aurate with those of chlorauric acid and of its potassium salt:



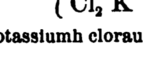
$$Au\left\{\begin{matrix} O \\ O\ K \end{matrix}\right.$$

Potassium aurate.



$$Au\left\{\begin{matrix} Cl_2 \\ Cl_2\ H \end{matrix}\right.$$

Chlorauric acid.



$$Au\left\{\begin{matrix} Cl_2 \\ Cl_2\ K \end{matrix}\right.$$

Potassiumh cloraurate.

Potassium chloraurate, $K\,Au\,Cl_4$ can be produced by mixing solutions of auric chloride and potassium chloride and evaporating to crystallization. Potassium bromoaurate, $K\,Au\,Br_4$, and potassium iodoaurate, $K\,Au\,I_4$, are also known.

Two sulphides of gold, aurous sulphide, $Au_2\,S$, and auric sulphide, $Au_2\,S_3$, are known. The former is produced by treating a solution of potassium *aurous* cyanide ($Au\,C\,N, K\,C\,N{=}K\,Au\,(C\,N)_2$) with hydrogen sulphide; the latter by precipitation from a cold neutral solution of auric chloride by means of hydrogen sulphide; if the solution is hot, nothing but metallic gold separates.*

The chief compounds discussed in the last chapter are given in the following table:

COMPOUNDS TYPICAL OF THE FAMILY, CORRESPONDING TO COMPOUNDS OF THE ALKALI METALS.

	Oxides.	Chlorides.	Sulphides.	
Copper, Silver, Gold,	$Cu_2\,O$ $Ag_2\,O$§ $Au_2\,O$§	$Cu\,Cl$* $Ag\,Cl$* $Au\,Cl$*	$Cu_2\,S$† $Ag_2\,S$† $Au_2\,S$†	Cuprous compounds. Argentic " Aurous "

* Insoluble in water.

† Insoluble in dilute acids.

The compounds of copper and silver unite with ammonia.

The salts of silver are derived from the oxide $Ag_2\,O$; for instance $Ag\,N\,O_3$, $Ag_2\,S\,O_4$.

§ Decomposed into oxygen and the metal when heated.

COMPOUNDS NOT TYPICAL.

	Oxides.	Hydroxides.	Chlorides.	Sulphides.
Cupric compounds Auric compounds	$Cu\,O$ $Au_2\,O_3$§	$Cu\,(O\,H)_2$ $Au\,(O\,H)_3$§	$Cu\,Cl_2$* $Au\,Cl_3$*§	$Cu\,S$ $Au_2\,S_3$§

The salts of copper are derived from cupric oxide; for instance $Cu\,(N\,O_3)_2$, $Cu\,S\,O_4$.

* Soluble in water.

§ Decomposed by heat, leaving gold behind.

Auric oxide is acidic in its character. It is also basic, for the few gold salts which are known (except $Au\,Cl$) are derived from it. The aurates are derived from the hydroxide $Au\,O_2\,H$; the salts derived from the alkalis are $Au\,O_2\,M$. Auric chloride has the character of an acidic anhydride; chlorauric acid, $Au\,Cl_4\,H$, chloraurates, $Au\,Cl_4\,M$.

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* A gold sulphide, $Au\,S$, is also described.

CHAPTER LIV.

THE FAMILY OF THE ALKALINE EARTHS.

Beryllium (Glucinum), symbol Be, atomic weight 9.
Magnesium, symbol Mg, atomic weight 24.3.
Calcium, symbol Ca, atomic weight 40.
Strontium, symbol Sr, atomic weight 87.6.
Barium, symbol Ba, atomic weight 137.

The elements comprising the primary group of the elements of the family ofalkaline earths are:

Beryllium,	atomic	weight	9 ,	specific	gravity	1.64,	atomic volume	5.6.
Magnesium,	"	"	24.3,	"	"	1.74,	" "	13.8.
Calcium,	"	"	40 ,	"	"	1.57,	" "	25 4.
Strontium,	"	"	87.6,	"	"	2.50,	" "	34.9.
Barium,	"	"	137 ,	"	"	3.75,	" "	36.5.

Of these, the first two, beryllium and magnesium, belong to the typical short periods and therefore resemble the following three, calcium, barium and strontium, but they also are closely allied with the three elements, zinc, cadmium and mercury, which comprise the secondary group belonging to this family. They *resemble* calcium, barium and strontium, because their oxides, hydroxides and the salts derived from them are formed according to the same formulæ; they *differ* from those three elements and fall into line with zinc, cadmium and mercury, by reason of the solubility of their sulphates[*] and because of their tendency to form double salts when their salts are brought in contact with those of ammonium.

Beryllium[†] and magnesium are prepared as metals by heating the chloride with metallic sodium:

$$M\,Cl_2 + 2\,Na = 2\,Na\,Cl + M.$$

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[*] The sulphates of calcium, strontium and barium are insoluble or nearly insoluble in water.

[†] Beryllium chiefly occurs as a metasilicate of beryllium and aluminium known as beryl, $Be_3\,Al_2\,(Si\,O_3)_6$. When these crystals are transparent and colored green by chromic oxide they are called emerald.

This method is exactly parallel to the one formerly employed in the preparation of aluminium (see page 322). The name glucinum was first given to beryllium owing to the sweetish taste of the salts of this metal.

Beryllium is white with a silver-like lustre, malleable and ductile; its melting point is lower than that of silver; it is slightly oxidized when heated to a high temperature; when finelv powdered and heated it burns with a brilliant light; it readily burns in an atmosphere of chlorine; dissolves in aqueous hydrochloric acid.

Magnesium is silver white, malleable and ductile, melts at 700°, is volatile at a high heat; the metal does not oxidize in dry air, but it readily corrodes in contact with water; when heated above its melting point in the air it burns with a most brilliant white light;* the metal also readily burns in chlorine; it is easily soluble in dilute acids.

Calcium, barium and strontium are isolated by electrolizing the fused chlorides in a crucible from which air is excluded; the positive electrode is made of gas carbon, which is not attacked by chlorine, the negative electrode consists of iron wire. This method is also employed in preparing the alkali metals. Calcium can also be made by reducing the iodide by means of metallic sodium.

Calcium, strontium and barium are yellow with metallic lustre. The freshly cut surfaces of the metals soon become covered with a layer of oxide; the metals must therefore be preserved under petroleum (see page 359). When heated in the air they burn with a brilliant light. They all energetically decompose water at ordinary temperatures

The changes which are brought about by the increasing atomic weights and volumes, as we pass downward in the list given above, are shown in the following table:

Beryllium does not decompose water.
Magnesium decomposes boiling water.
Calcium " water at ordinary temperatures.
Strontium " " very readily at ordinary temperatures.
Barium " " as readily as the alkali metals.

The oxides and hydroxides which are typical of the family have the formulæ M O and M $(O\ H)_2$; the metals are therefore divalent and replace two atoms of hydrogen in acids.

	Oxides		Hydroxides.
Beryllium	Be O	Not changed to hydroxide by the addition of water	Be $(O\ H)_2$
Magnesium	Mg O	Slowly " " " " " " " "	Mg $(O\ H)_2$
Calcium	Ca O	Readily " " " " " " " "	Ca $(O\ H)_2$
Strontium	Sr O	" " " " " " " " "	Sr $(O\ H)_2$
Barium	Ba O	" " " " " " " " "	Ba $(O\ H)_2$

The hydroxides of beryllium and of magnesium are insoluble in water. The solubility of the other three *increases* with increasing atomic weight (see pages 359 and 360), while the stability increases with the solubility.

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* This magnesium light is rich in actinic rays and is used as a flash light in photography.

$Be\,(O\,H)_2$ decomposes at about 300°; $Be\,(O\,H)_2 = Be\,O + H_2\,O$.
$Mg\,(O\,H)_2$ “ “ a low red heat; $Mg\,(O\,H)_2 = Mg\,O + H_2\,O$.
$Ca\,(O\,H)_2$ “ “ a high red heat; $Ca\,(O\,H)_2 = Ca\,O + H_2\,O$.
$Sr\,(O\,H)_2$ “ “ a white heat; $Sr\,(O\,H)_2 = Sr\,O + H_2\,O$.

$Ba\,(O\,H)_2$, which crystallizes from water in crystals of the formula $Ba\,(O\,H)_2 + 8\,H_2\,O$, and which is quite soluble in water, can be fused without change.

The oxides and hydroxides are all strong bases; the solutions of calcium, strontium and barium hydroxides have an alkaline reaction. The hydroxide of beryllium, being that of the least metallic of all the elements, can also dissolve in caustic alkalis, so that under certain circumstances, it acts as an acid. The oxide and hydroxide of calcium, known respectively as quick and slaked lime, are the most important of these compounds.

Calcium oxide is prepared by heating the carbonate in "lime kilns" until it decomposes into calcium oxide and carbon dioxide:

$$Ca\,C\,O_3 = Ca\,O + C\,O_2.$$

The quick lime so prepared is more or less impure, according to the condition of the limestone or marble used; when brought in contact with water it unites with that liquid to form calcium hydroxide (or slaked lime); at the same time a large amount of heat is developed:

$$Ca\,O + H_2\,O = Ca\,(O\,H)_2.$$

If quick lime is exposed to the air it absorbs carbon dioxide and water. It then crumbles and is said to be "air slaked."

Slaked lime finds its chief use in the preparation of mortar. *Mortar* is prepared by stirring together slaked lime and sand until the mass assumes the consistency of thick porridge. When placed between bricks the mixture gradually hardens, the calcium hydroxide absorbing carbon dioxide and changing into calcium carbonate. The sand, which is added, in all probability serves the purpose of rendering the mortar porous, and it thereby facilitates the absorption of carbon dioxide; it certainly does not, as was formerly supposed, render the product hard by forming calcium silicate. A mixture of quick lime, aluminium oxide and silicon dioxide forms Portland cement. The latter, when brought in contact with water, gradually hardens, owing to the union of the calcium and aluminium oxides with the silicon dioxide which is present. The chemical process depends upon the formation of hydrated calcium silicates as well as of calcium aluminate.

Barium superoxide.—In addition to the ordinary oxide, $Ba\,O$, barium is also able to form a *hyperoxide*, $Ba\,O_2$ (see pages 49 and

312). This compound is prepared by passing oxygen over barium oxide which is heated to redness, or by heating a mixture of barium oxide and potassium chlorate. The substance is a greyish powder which loses oxygen at a bright red heat. It is a powerful oxidizer; hydrogen, boron, carbon, sulphur, etc., are changed to the corresponding oxides when heated with it; in many cases the temperature of the mass even spontaneously increases to redness during the process. Barium hyperoxide, when mixed with cold water, forms a hydrate, $Ba\,O_2 + 6\,H_2\,O$; boiling water decomposes it, liberating oxygen and leaving barium hydroxide. Barium hyperoxide forms hydrogen peroxide (see page 49) when treated with dilute acids:

$$Ba\,O_2 + 2\,H\,Cl = Ba\,Cl_2 + H_2\,O_2.$$

In this respect barium hyperoxide differs radically from other hyperoxides, for the latter liberate chlorine when in contact with hydrochloric acid (see pages 58 and 312). The cause of this difference lies in the fact that the hyperoxides of manganese and lead form intermediary compounds before setting free the halogene.

The chlorides of the elements of this family, $M\,Cl_2$, are all soluble in water; those of beryllium and magnesium decompose when heated in a current of air, giving off chlorine and leaving the oxide; the chlorides of calcium, barium and strontium are more stable. *The chloride of calcium* $Ca\,Cl_2 + 6\,H_2\,O$, melts in its water of crystallization at 29°; at 100° it becomes anhydrous and then again melts; this fused form of calcium chloride is deliquescent and, because it greedily absorbs moisture, is frequently used as a drying agent. *The chloride of strontium* is not deliquescent, while *the chloride of barium* slowly takes up water from the air. *The bromides and iodides* are like the chlorides in every respect. The chlorides of calcium and of magnesium occur as minerals in some salt deposits, the former as chlorocalcite, the latter as the extremely deliquescent mineral bischofite. Carnallite is a double chloride of potassium and magnesium, $K\,Cl, Mg\,Cl_2 + 6\,H_2\,O$, which occurs quite frequently in the Strassfurth salt regions. The increasing metallic character of the elements of this family with increasing atomic weight is very well illustrated by the behavior of the chlorides in the presence of water:

$Be\,Cl_2 + 4\,H_2\,O$. completely decomposed into $Be\,O + 2\,H\,Cl$ when its solution is evaporated.

$Mg\,Cl_2 + 6\,H_2\,O$, completely decomposed into $Mg\,O + 2\,H\,Cl$ when its solution is evaporated.

$Ca\,Cl_2 + 6\,H_2\,O$, partly decomposed into basic calcium chloride when heated with water.

$Sr\,Cl_2 + 6\,H_2\,O$, not decomposed.

$Ba\,Cl_2 + 2\,H_2\,O$. not decomposed.

All of of the carbonates of the members of this family are insoluble in water. They are the more stable the more positive the metal forming them is, so that their stability increases as the atomic weights of the elements, counting from above downward, become greater. Beryllium carbonate is only capable of existence as a normal salt when it is in an atmosphere of carbon dioxide; when exposed to the air it breaks down, giving off carbon dioxide and leaving a basic carbonate; magnesium carbonate begins to break down at 100°; calcium carbonate at a low red heat, while strontium and barium carbonates do not decompose until a white heat is reached. All of the carbonates can be prepared by precipitation from solutions of the salts of the respective metals by addition of a soluble carbonate, such as that of sodium. The following will serve as examples:

$$\underbrace{\begin{array}{lll} Na_2\,C\,O_3 & + Ba\,Cl_2 & = 2\,Na\,Cl \\ K_2\,C\,O_3 & + Ca\,Cl_2 & = 2\,K\,Cl \\ (N\,H_4)_2\,C\,O_3 & + Mg\,Cl_2 & = 2\,N\,H_4\,Cl \end{array}}_{\text{Soluble.}} \begin{array}{l} + \\ + \\ + \end{array} \underbrace{\begin{array}{l} Ba\,C\,O_3 \\ Ca\,C\,O_3 \\ Mg\,C\,O_3 \end{array}}_{\text{Insoluble.}}$$

The carbonates of magnesium, calcium, strontium and barium, and the double carbonate of magnesium and calcium form an extremely important dimorphous and isomorphous group of minerals, in some localities entire mountain ranges are made up of these compounds, while the various amorphous and cryptocrystalline varieties of calcium carbonate known as chalk, limestone and marble constitute deposits of astonishing magnitude (see page 281). The following table gives the relationship between the crystalline carbonates of the elements belonging to this family:

HEXAGONAL SYSTEM, RHOMBOHEDA. *Calcite group,*		RHOMBIC SYSTEM. *Arragonite group.*
Calcite (calcspar)	$Ca\,C\,O_3$	Arragonite.
Magnesite	$Mg\,C\,O_3$	
Dolomite	$Ca\,C\,O_3$, $Mg\,C\,O_3$	
	$Ba\,C\,O_3$	Witherite.
	$Sr\,C\,O_3$	Strontianite.

While magnesium carbonate is not, by itself, capable of crystallizing in the same form as arragonite, yet, when mixed with the carbonates of manganese and calcium, it assumes that form; on the other hand, calcite crystals which contain barium and strontium are also found. This isomorphous group of minerals is very far reaching, for the carbonates of zinc, iron, manganese and cobalt also belong to the calcite group, while those of manganese, iron and lead are also found crystallizing in the form of arragonite.

The sulphates of the elements of this family can be divided into two classes, those of beryllium and magnesium, which are soluble in water, and those of calcium, strontium and barium. Of the latter, that of calcium is soluble with difficulty, that of strontium is less soluble than that of calcium, while the sulphate of barium is insoluble; these sulphates can therefore be produced as white precipitates on the addition of a soluble sulphate to the solutions of salts of the respective metals.*

Magnesium sulphate is the representative of a large number of sulphates which are known as vitriols. The vitriols, with the exception of copper sulphate, which contains five molecules of water, all crystallize with seven molecules of water of crystallization and form a typical isomorphous group of compounds; the one exception, copper sulphate, $Cu\,S\,O_4 + 5\,H_2\,O$, can, however, crystallize with seven molecules of water when it is present in *an isomorphous mixture with some other vitriol.* The vitriols, when heated to 100°, change to salts having the composition $M\,S\,O_4 + H_2\,O$; the last remaining molecule of water passes off at a higher temperature, and for this reason these substances are commonly regarded as being secondary salts of the hydrated sulphuric acid, $H_4\,S\,O_5$, so that their formulæ would be $M\,H_2\,S\,O_5 + 6\,H_2\,O$. The following is a list of the compounds comprising this isomorphous group:

$Be\,H_2\,S\,O_5 + 6\,H_2\,O$, beryllium sulphate.
$Mg\,H_2\,S\,O_5 + 6\,H_2\,O$, magnesium sulphate.
$Zn\,H_2\,S\,O_5 + 6\,H_2\,O$, zinc sulphate (white vitriol).
$Fe\,H_2\,S\,O_5 + 6\,H_2\,O$, ferrous sulphate (green vitriol).
$Ni\,H_2\,S\,O_5 + 6\,H_2\,O$, nickel sulphate.
$Co\,H_2\,S\,O_5 + 6\,H_2\,O$, cobalt sulphate.
$Cu\,H_2\,S\,O_5 + 4\,H_2\,O$, copper sulphate (blue vitriol), the latter crystallizing with six molecules of water when in an isomorphous mixture. All of the vitriols can crystallize with one formula weight of potassium or of ammonium sulphate to form double salts of the general formula $M_2\,S\,O_4, M\,S\,O_4 + 6\,H_2\,O$.

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*Calcium sulphate will not be precipitated if the solution of the calcium salt is too dilute. A solution of calcium sulphate will precipitate strontium and barium salts; a solution of strontium sulphate will precipitate barium salts.

Calcium, strontium and barium sulphates occur quite frequently as minerals, constituting an isomorphous group belonging to the rhombic system, the representatives of which are given in the following table:

Anhydrite, $Ca\ S\ O_4$.
Celestine, $Sr\ S\ O_4$.
Barite, $Ba\ S\ O_4$.
Barytocelestine, $(Ba, Sr)\ S\ O_4$.
Anglesite, $Pb\ S\ O_4$.

Calcium sulphate also occurs as gypsum, crystallized with two molecules of water of crystallization, $Ca\ S\ O_4 + 2\ H_2\ O$; the latter substance is frequently found as a massive variety, in which condition it bears the name of alabaster. When gypsum is heated to a little above 100° it loses its water of crystallization and is converted into a fine white powder known as plaster of Paris; this substance, mixed with water, once more unites with the latter and changes into a firm mass which has the composition of alabaster; this process is termed the "setting" of plaster of Paris. Many natural waters contain calcium sulphate in solution; such waters are known as permanent hard waters, because the calcium salt is not removed from them by boiling. Temporary hard waters contain primary calcium carbonate, $Ca\ (H\ C\ O_3)_2$; the latter substance, however, breaks down into carbon dioxide and insoluble calcium carbonate when the solution is boiled; the calcium salt is therefore entirely removed by this process. Calcium is able to form an insoluble compound with soap; hard waters, therefore, form a precipitate when brought in contact with the latter substance, and will consequently only form a lather after all the calcium salts have been removed (see page 280).

The tertiary and secondary phosphates of the elements belonging to this family are all insoluble in water; the primary phosphates are soluble; as a consequence, the tertiary phosphates are dissolved on addition of the stronger acids, such as hydrochloric or nitric. The tertiary phosphate of calcium is the only one of these which occurs as a mineral, being known as phosphorite or osteolite, $Ca_3\ (P\ O_4)_2$, often found in massive deposits which are especially extensive in Florida; guano is tertiary calcium phosphate which is mixed with a number of impurities, such as calcium carbonate, magnesium carbonate, gypsum, etc. A double salt of calcium phosphate and calcium chloride is found in crystals belonging to the hexagonal system and is called apatite, $Ca_3 (PO_4)_2 + CaCl_2$. In addition to the mineral occurrences, calcium phosphate is the chief constituent of the inorganic portions of the bones (see page 203), of the ashes of which it forms 85 per cent. The reactions relating to the conversion of the tertiary phosphate into the soluble primary one are given on pages 219 and 220. The soluble primary phosphate of calcium, mixed with gypsum and other impurities, is called superphosphate and is used as a foundation for the mixtures which find their way into the market as artificial fertilizers; of course the phosphate must be in a soluble form in order to be readily absorbed by plants; this conversion of the tertiary into the primary phosphate is effected by means of sulphuric acid:

$$Ca_3 (PO_4)_2 + 2 H_2SO_4 = Ca (H_2PO_4)_2 + 2 CaSO_4.$$

The value of a fertilizer is determined by the amount of soluble phosphate which it contains.

Magnesium phosphate behaves exactly as does calcium phosphate, the tertiary, secondary and primary phosphate being known; the latter is soluble in water. The most important phosphate of magnesium is the insoluble ammonium magnesium phosphate, $Mg (NH)_4 PO_4$; the formation of this as a precipitate may be used as a test either for the presence of magnesium or of phosphoric acid in a solution. The salt is produced by adding a soluble phosphate to a mixture of a soluble magnesium salt with ammonia and ammonium chloride. If ammonia alone were added to a solution containing a magnesium salt, a portion of the latter would be decomposed and the base precipitated as magnesium hydroxide, while a part would remain in solution as a double salt of magnesium and ammonium, for magnesium salts have the power of forming compounds with ammonium salts and these compounds are not decomposed by ammonia:

$$2 MgSO_4 + 2 NH_3 + 2 H_2O = Mg (OH)_2 + (NH_4)_2SO_4, MgSO_4.$$

The previous addition of an ammonium salt to a solution containing a salt of magnesium therefore prevents any precipitation of magnesium hydroxide by means of ammonia. When ammonium-magnesium phosphate is heated it loses ammonia and changes into the *secondary* phosphate of magnesium:

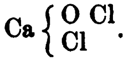
$$MgNH_4PO_4 = MgHPO_4 + NH_3,$$

and the latter on further heating loses water and leaves magnesium pyrophosphate (see page 220):

$$2\,Mg\,H\,P\,O_4 = Mg_2\,P_2\,O_7 + H_2\,O.$$

Arsenic acid reacts similarly to phosphoric acid. It forms an ammonium-magnesium arsenate, $Mg\,N\,H_4\,As\,O_4$. The precipitate formed is not to be distinguished from ammonium-magnesium phosphate; if both arsenic and phosphoric acid are present in solution the arsenic acid must, therefore, previous to precipitation, be reduced to arsenious acid by means of sulphur dioxide.

The hypochlorite of calcium when mixed with calcium hydroxide and calcium chloride is known as chloride of lime. Because of the invariable occurrence of calcium chloride in conjunction with calcium hypochlorite, the theory is not infrequently maintained that calcium hypochlorite is in reality a mixed chloride and hypochlorite of calcium having the formula:



$$Ca\left\{\begin{matrix}O\,Cl\\ Cl\end{matrix}\right. .$$

Such a body would have the same composition by weight as an equimolecular mixture of calcium chloride and calcium hypochlorite, $Ca\,Cl_2 + Ca\,(O\,Cl)_2 = 2\,Ca\,(O\,Cl)\,Cl$. The reactions peculiar to calcium hypochlorite have been explained on pages 116 and 117.

The chlorates and nitrates of calcium, barium and strontium are soluble in water and are extensively used in the manufacture of Greek fire; the chlorate of strontium when mixed with oxidizable substances and ignited, gives an intensely red light, while that of barium produces a green one.

The silicates of calcium are of the greatest importance because of the fact that they are essential to the manufacture of glass. Calcium metasilicate, $Ca\,Si\,O_3$, occurs as the mineral wollastonite, and a great many other naturally occurring silicates contain calcium (see page 296); these silicates are, however, crystalline in their structure, while the artificial silicates are, as a rule, amorphous. Glass consists of a vitreous mixture of the silicates of the alkalis and of calcium with silicon dioxide; in some forms of glass, however, lead oxide may replace calcium oxide. Ordinary window glass is produced by fusing sand, calcium carbonate and sodium carbonate together, the silicate of calcium and sodium so formed is, in reality, of a crystalline structure, but the latter is concealed by the vitreous mass of silicon dioxide; such a glass is readily attacked by reagents and even by the continued action of water and after it has been attacked for some time the crystalline condition becomes apparent. *Window glass* is first blown and then cut into suitable pieces; for that reason it is more or less irregular in thickness and does not present a perfectly smooth surface. *Plate glass* has essentially the same composition, but is cast on flat plates and finally polished. *Bohemian glass* is made by fusion of potassium carbonate, a little sodium carbonate, silicon dioxide and calcium carbonate. The replacing of the sodium carbonate by potassium carbonate, with the resulting formation of a potassium-calcium silicate, renders the glass difficultly fusible. Bohemian glass is used for the manufacture of chemical apparatus, a further advantage belonging to this variety being in the fact that it is not readily attacked by chemical reagents. *Bottle glass* contains more calcium silicate than either of the above varieties; it is frequently colored green by the presence of ferrous silicate. The commoner bottles are made from impure materials. *Flint glass* is of similar composition to ordinary lime-soda glass with the exception that the lime is replaced by lead oxide; it is characterized by having a very high index of refraction,* bright lustre and high specific gravity; it is the most fusible variety of glass.† Flint glass is used in the manufacture of optical instruments and in some chemical apparatus. *Strass* is flint glass which is very rich in lead; it is used for making artificial gems. Glass is stained by adding inorganic coloring matter; thus, blue glass is produced by adding a little cobalt salt, green glass by copper and chromium, etc. The various glass utensils which are used must be previously annealed by a very slow cooling process; if this precaution is not taken, the outer surfaces, cooling more rapidly than the remainder of the mass, establish such a tension that the slightest scratch upon the surface will cause the entire object to be shattered. This condition is best shown in the so-called Prince Rupert's drops. The latter are made by fusing glass and allowing the drops to fall into water; when the end of the small pear-shaped mass so formed is broken, the drop disintegrates into a sandy mass with explosive violence.

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* The index of refraction for flint glass is 1.8, while that of window glass is 1.53.

† In working with lead glass care must be taken not to bring the same into the reducing flame (see page 271), which is that portion immediately outside of the central zone, otherwise a part of the lead silicate will be reduced and lead will separate; the latter renders the glass black and opaque.

CHAPTER LV.

ZINC, CADMIUM AND MERCURY.

Zinc, symbol Zn, atomic weight 65.3.
Cadmium, symbol Cd, atomic weight 112.
Mercury, symbol Hg, atomic weight 200.

Zinc, cadmium and mercury form the secondary group of the family of the alkaline earths. They are the second elements of the second halves of the long periods, while calcium, strontium and barium occupy the same position in the first halves. As a consequence they bear much the same relationship to the alkaline earths as copper, silver and gold bear to the alkalis. The typical oxides and hydroxides as well as the salts derived from the latter are therefore of the same formula when formed of zinc, cadmium and mercury as they are with calcium, strontium and barium. In both divisions of the family the metals are divalent, so that the oxides have the general formula $M\,O$ and the hydroxides $M\,(O\,H)_2$.

In their physical characteristics the three elements are all, most certainly, metallic in their nature but zinc, the one with the least atomic weight,* is less positive than the other two. The change in physical character brought about by the increasing atomic weight, as we pass from zinc to mercury, is shown in the following table:

Zinc,	atomic weight	65.3,	specific gravity	7.15,	atomic volume	9.1,	melting point	417°.
Cadmium,	“ “	112,	“ “	8 65,	“ “	12.9,	“ “	317°.
Mercury,	“ “	200,	“ “	13.59,	“ “	14.7,	“ “	—39°.

All three of the metals are volatile; their boiling points decrease with increasing atomic weight, just as their melting points do; this phenomenon, which is most strikingly illustrated in the case of the trio of metals under discussion, is exactly the reverse of the changes in the melting points taking place in the not-metallic families at the right hand extremities of the periods. It will be remembered, also, that the melting points of the alkali metals diminish as we pass from member to member in the direction of increasing atomic weights, and the same is true of the metals constituting the first portion[*] of the family under discussion; the elements, therefore, which comprise the first two families, show decreasing melting points with increasing atomic weights; whether the same is true of the boiling points cannot be stated, as many of the elements cannot be volatilized by any of the means at our command; it certainly is true of the three metals under consideration, for:

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* Zinc is also the element with the next lower atomic weight to that of gallium, which element has many of the characteristics of a not-metal; we would therefore scarcely expect zinc to present very marked metallic properties.

Zinc boils at 927°.
Cadmium " " 772°.
Mercury " " 357°.

Zinc is an element with a brilliant metallic lustre which possesses a bluish tint and a crystalline structure.[†] It is only malleable at temperatures between 100° and 150°; at ordinary temperatures it is easily fractured; at 200° the metal can readily be pounded into a powder; when heated to its point of vaporization in the air, zinc burns with a bluish white flame, producing zinc oxide, $Zn\,O$. The metal easily dissolves in dilute acids (see pages 30, 198). Solutions of the caustic alkalis, when warmed, attack zinc, forming zincates and liberating hydrogen; in this respect zinc resembles aluminium and a number of other metals which can display both metallic and not-metallic properties; this behavior is not unexpected when we consider that zinc is the element with least metallic properties in the group we are considering and that *every other element following it in the same period also can display not-metallic properties.*

Cadmium is a glistening, tin-like metal; it is soft, though harder than tin, and it has a crystalline structure; when heated to its boiling point in the air, it burns like zinc, forming cadmium oxide, $Cd\,O$. The metal dissolves in acids less readily than does zinc, but with this exception shows the same behavior. The metal *does not dissolve in solutions of the caustic alkalis.*

Mercury is a bluish white metal which is fluid under ordinary circumstances. The solid substance (formed at —39°) is soft and malleable when pure. Mercury is not changed in the air at ordinary temperatures; if heated for some time near its boiling point and in the presence of oxygen, it is changed to red mercuric oxide, Hg O; ozone readily attacks it without the necessity of heating. Hydrochloric acid or dilute sulphuric acid do not dissolve mercury; concentrated sulphuric acid, when hot, attacks the metal and liberates sulphur dioxide; nitric acid, concentrated or dilute, acts upon mercury; if the acid is dilute, mercurous nitrate is formed, if concensrated, mercuric nitrate is produced; alkalis do not attack mercury.

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[*] Beryllium, magnesium, calcium, strontium and barium have decreasing melting points as we pass along the line in the order named. The melting points of calcium and strontium are not accurately determined.

[†] When pieces of zinc are bent a peculiar crepitation, similar to that of tin, is observed (see page 302).

As has been stated, zinc, cadmium or mercury can be easily volatilized. The specific gravities of their vapors are as follows:

Zinc, specific gravity of vapor, air = 1, 2.36, H = 2, 67.96; molecular weight, 65.3.
Cadmium, " " " " air = 1, 3.94, H = 2, 113.47; " " 112.
Mercury, " " " " air = 1, 6.83, H = 2, 197. ; " " 200.

The above determinations show that the molecular weight and the atomic weight of each of the three elements, when in the state of a vapor, are identical. Zinc, cadmium and mercury, therefore, in changing from the liquid to the gaseous state, separate at once into the individual atoms, provided our decision as to what the weights of these atoms are, is the correct one; the only other elements which exhibit the same phenomenon are sodium and potassium (and iodine when heated above 1500°; below that temperature the molecules of iodine are formed of two atoms [see page 80]). In the course of our study we have therefore encountered elements with one, with two, with three and with four atoms united to form a molecule of the gas, the molecules having three and four atoms are, however, dissociated at high temperatures and then change into those having two, while some of the latter have already been dissociated into the individual atoms. Undoubtedly, were we able to command a sufficiently high temperature in the apparatus used for determining the vapor densities, we would be able to finally change all of the diatomic molecules into monatomic ones. The following gives a list of elements of which it has been possible to obtain specific gravities while they were in the gaseous state; in the cases of selenium and antimony some doubt exists as to whether the molecules are, in reality, triatomic or whether the vapor density numbers which have been obtained are only accidental.

MONATOMIC.*	DIATOMIC.	TRIATOMIC.	TETRATOMIC.
Sodium	Hydrogen	Ozone	Phosphorus
Potassium	Chlorine	Selenium (?)	Arsenic
Zinc	Bromine	Antimony (?)	
Cadmium	Iodine (below 600°)		
Mercury	Oxygen		
Iodine (above 1500°)	Sulphur		
Bismuth (?)	Selenium		
	Tellurium (?)		
	Nitrogen		
	Phosphorus Arsenic } at white heat		

The fact that so many elementary gases are formed of complex molecules was not understood when the theory that equal volumes of gases contain equal numbers of particles was first advanced; the discrepancy frequently observed between the specific gravity of the gases and the atomic weights of elements determined by other means, therefore, led to a disbelief in Avogadro's hypothesis and to considerable confusion in the determination of atomic weights.

The principal minerals in which zinc, cadmium and mercury occur are as follows:

Zinc and cadmium.—The occurrence of uncombined zinc as a mineral is doubtful. Zinc and cadmium occur as the sulphides, $Zn\,S$ and $Cd\,S$, in an isomorphous and dimorphous group which also includes the sulphides of manganese, iron and nickel. The sulphide of zinc occurs in crystals belonging to the regular system called sphalerite or zinc-blende and in hexagonal crystals called wurtzite. The sulphide of cadmium is isomorphous with wurtzite and is known as greenockite. Zinc further is sometimes found as zincite, which is the oxide, $Zn\,O$, colored red by means of manganese. The carbonate of zinc, $Zn\,C\,O_3$, smithsonite, is isomorphous with calcite (see page 393). An aluminate of zinc, $Zn\,(Al\,O_2)$, isomorphous with spinell (see page 326), is also met with.

Mercury is sometimes found in small, fluid globules in places where the most important mineral containing mercury, namely the red sulphide, cinnabar, $Hg\,S$, also occurs. In addition, amalgams of mercury with silver and gold are sometimes met with.

Zinc is obtained from its ores by roasting the sulphide in a draught of air and by subsequently heating the oxide so produced with charcoal. As zinc is volatile at no very high temperature, the mixture of oxide and charcoal is placed in earthenware retorts which are gradually heated; carbon monoxide passes off during this process:

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* It seems scarcely necessary to state that the term monatomic means existing as molecules formed of one atom, diatomic of two, etc.

$$ZnO + C = Zn + CO.$$

Finally, the temperature is increased to a point at which zinc begins to distill; earthenware receivers are then placed before the openings of the retorts and the metal is collected therein. The first portions which pass over are deposited on the walls of the receivers in the form of a fine dust which always contains more or less oxide of zinc; this product, which is known as zinc-dust, is very frequently used as a reducing agent in the laboratory. The fused zinc which finally collects is generally impure, containing lead, iron and cadmium; it is separated from these by repeated distillation. The cadmium, having a lower boiling point, passes over first, while the lead and iron remain behind. *The preparation of cadmium* is like that of zinc. As cadmium ores generally contain zinc, the metal is separated from the latter by distillation. *Mercury is obtained* by roasting the sulphide, the mercury which passes off being collected in receivers which are connected with the oven. The addition of charcoal is unnecessary during this process, because the oxide of mercury which would be formed by roasting the sulphide is further decomposed into mercury and oxygen by heat (see page 18).

As has been mentioned, zinc is a constituent of the alloy known as brass. When sheet-iron is covered with a layer of zinc it is known as galvanized iron. Zinc readily forms an amalgam with mercury; an extensive commercial use of this fact is made in amalgamating zinc battery plates, the latter being cleaned, dipped in acid and rubbed with mercury so as to produce a thin layer. Cadmium, zinc and mercury form an amalgam which readily hardens; the latter is used as an amalgam filling for teeth. Alloys of cadmium with lead and bismuth are used where a very low-melting metal is required. Alloys of mercury are termed *amalgams;* a number of these have definite composition and crystalline form. The nature of amalgams has been discussed on page 240.

Zinc and cadmium form but one oxide apiece; these oxides in formula correspond to the typical oxide of the family, MO. The hydroxides, $M(OH)_2$, can be produced by adding soluble hydroxides to solutions containing salts of cadmium or zinc;

$$MCl_2 + 2KOH = 2KCl + M(OH)_2,$$

however, in adding a caustic alkali to a zinc salt, care must be taken not to use an excess of the reagent, for zinc hydroxide acts as an acid when in the presence of strong bases, as it dissolves in the latter to form *zincates:*

$$Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O.$$

(See pages 304 and 326); the zincate so formed is, however, decomposed by boiling, zinc hydroxide being precipitated; ammonia water has the same effect as solutions of the caustic alkalis, an excess of that reagent dissolving the precipitated hydroxide while producing ammonium zincate.* Acid solutions of zinc salts, or mixtures of ammonium and zinc salts, are not affected by ammonia. In the case of cadmium, caustic alkalis precipitate the hydroxide, which, however, is not dissolved by an excess of the reagent, cadmium hydroxide having no acid properties; on the other hand, ammonia, when in the presence of ammonium salts, produces no precipitate, for cadmium resembles zinc and magnesium in the facility with which its salts form compounds with those of ammonium.

ZnO is a white powder; yellow when heated.

CdO is a brown powder.

$Zn(OH)_2$ is a white powder; changes to $ZnO + H_2O$ when heated.

$Cd(OH)_2$ is a white powder; changes to $CdO + H_2O$ when heated.

In addition to the methods which have been given above, the oxides can be produced by heating the respective carbonates or nitrates.

The chloride of zinc can be produced by heating zinc in a current of chlorine, or by dissolving zinc, or the oxide or hydroxide of the metal, in hydrochloric acid, evaporating the solution and distilling. The fused salt is cast into sticks which are extremely deliquescent. The salt crystallizes from a concentrated solution of hydrochloric acid in crystals of the formula $ZnCl_2 + H_2O$. When the aqueous solution is evaporated a partial decomposition into the basic chloride takes place:

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* Difference between zinc and magnesium, for ammonia precipitates a portion of the magnesium as magnesium hydroxide. The latter is insoluble in an excess of the reagent (see page 396).

$$Zn\left\{\begin{matrix}Cl\\Cl\end{matrix}\right. + HOH = Zn\left\{\begin{matrix}OH\\Cl\end{matrix}\right. + HCl.$$

The latter substance, when heated with water, finally loses all chlorine and changes to the hydroxide (see magnesium chloride, pages 392, 393). The chloride of cadmium, $CdCl_2$, is similar to that of zinc; like zinc chloride it is volatile, but is not decomposed when the solution is evaporated.

Zinc sulphate, formed by dissolving either the hydroxide, oxide, carbonate or the metal in sulphuric acid, belongs to the class of sulphates which are termed vitriols (see page 394). Like all of the sulphates belonging to this group, it is soluble in water and crystallizes with seven molecules of water, six of which it loses at 100°, while the seventh only passes off at a higher temperature.

Cadmium sulphate does not belong to the group of vitriols. Its crystals have the formula $3\,CdSO_4 + 8\,H_2O$.

When a solution of the carbonate of an alkali metal or of ammonium is added to the solution of a zinc salt, an insoluble *basic carbonate of zinc is precipitated.* This substance has a varying composition, according to the conditions under which it is produced. The normal *secondary carbonate* of zinc, $ZnCO_3$, occurs as the mineral smithsonite, belonging to the calcite group. The carbonate is easily decomposed into zinc oxide and carbon dioxide when heated.

Cadmium carbonate is precipitated from solutions containing a cadmium salt by addition of a soluble carbonate. Owing to the more metallic nature of cadmium, the precipitate so formed consists of the secondary carbonate, $CdCO_3$.

Zinc sulphide is precipitated from the neutral or alkaline solutions of zinc salts by addition of either hydrogen sulphide or of a soluble alkaline sulphide.* When so precipitated it forms a white

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* If the zinc salt is the salt of a strong acid, such as hydrochloric, nitric or sulphuric, a portion of the zinc only is precipitated as the sulphide, for, as will be seen from the following reaction, a portion of the acid is set free and the compound so formed decomposes the precipitated sulphide in order to once more form a soluble salt of zinc:

$$ZnSO_4 + H_2S = ZnS + H_2SO_4$$
$$ZnS + H_2SO_4 = ZnSO_4 + H_2S.$$

This difficulty is not encountered if the zinc salt of a weak acid is used or if ammonia is previously added so as to neutralize any acid which may be liberated.

powder; in a crystalline state it is found as zinc-blende, a substance having much the same color as ordinary resin.

Cadmium sulphide is precipitated from solutions of cadmium salts, even if the latter are slightly acid, for the substance is insoluble in dilute acids. The precipitate is yellow in color.

Mercury forms two classes of compounds, *mercurous* compounds, derived from the metal in its monovalent state, and *mercuric* compounds, derived from divalent mercury. The same distinction, it will be remembered, existed between *cuprous* and *cupric* derivatives.

Oxides of mercury: Mercurous oxide, Hg_2O, mercuric oxide, HgO. The former is produced by adding potassium hydroxide to a solution of mercurous nitrate, the hydroxide, which would be expected, at once breaking down into water and the oxide:

1. $2\,HgNO_3 + 2\,KOH = 2\,KNO_3 + 2\,HgOH$,
2. $2\,HgOH = Hg_2O + H_2O$.*

Mercurous oxide is a black powder which is quite unstable; when exposed to the light it breaks down into mercury and *mercuric* oxide:

$$Hg_2O = Hg + HgO.\dagger$$

Addition of acids produces *mercurous* salts; oxidizing agents change mercurous compounds into mercuric compounds.

Mercuric oxide exists in two forms, according to the method of its preparation; the one is red and of crystalline structure, the other is yellow and amorphous. *The red oxide* can be prepared either by heating mercury to just below its boiling point in the presence of oxygen, when after a long time it becomes covered with crystalline scales of the substance sought, or by heating mercuric nitrate, which salt breaks down into mercuric oxide and nitrogen peroxide (see page 199):

$$Hg(NO_3)_2 = HgO + 2\,NO_2.$$

The yellow oxide of mercury is produced by precipitating from

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* It will be remembered that the same is true of the formation of the oxide of silver; when a soluble hydroxide is added to the solution of a silver salt, not the hydroxide, *but the oxide*, is precipitated:

$$2\,AgNO_3 + 2\,KOH = 2\,KNO_3 + Ag_2O + H_2O.$$

† This change reminds us of the ones which we encountered with many of the oxides and acids of the not-metals.

solutions of mercuric salts by the addition of a soluble hydroxide, the hydroxide at once breaking down into the oxide and water:

1. $Hg(NO_3)_2 + 2KOH = Hg(OH)_2 + 2KNO_3$.
2. $Hg(OH)_2 = HgO + H_2O$.

Both varieties of mercuric oxide turn black when heated; they resume their usual color after cooling; at a dull red heat they decompose into mercury and oxygen (see page 18); sunlight has the same effect as heat. When mercuric oxide is treated with an acid it produces *mercuric* salts. All soluble mercury compounds, as well as the metal itself, are extremely poisonous. Under certain circumstances mercuric oxide displays slightly acidic properties, so, for instance, it is attacked, in small quantities, by fused potassium hydroxide.

Chlorides of mercury: Mercurous chloride (calomel), $HgCl$, mercuric chloride (corrosive sublimate), $HgCl_2$. *Mercurous* chloride sometimes occurs in a crystalline form as a mineral. Mercurous chloride can either be prepared by heating mercuric chloride with a sufficient quantity of mercury,*

$$HgCl_2 + Hg = 2HgCl,$$

or by adding hydrochloric acid or a soluble chloride to a solution containing a mercurous salt, for mercurous chloride is insoluble in water or dilute acids:

$$HgNO_3 + HCl = HgCl + HNO_3,$$
$$HgNO_3 + NaCl = HgCl + NaNO_3.$$

In this respect, then, mercurous compounds are much like those of silver; indeed all of the monovalent heavy metals act alike in producing insoluble chlorides.†

Mercurous chloride, when heated, evaporates without previously melting. The specific gravity of the vapor is 8.01; the calculated specific gravity for a gas composed of molecules of the formula $HgCl$ is 8.14; in this respect mercurous chloride differs from cuprous chloride, for the vapor density of the latter compound leads

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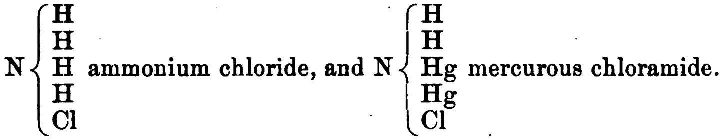
[*] This operation must be carried on in large flasks stoppered with chalk. The calomel then sublimes from the lower part of the flask and collects on the cooler portions. If the vessel is too small, a portion of the mercury salt will evaporate.

[†] Cuprous chloride, $CuCl$, argentic chloride, $AgCl$, aurous chloride, $AuCl$, mercurous chloride, $HgCl$, and thallous chloride, $TlCl$, are insoluble.

to a formula $Cu_2\,Cl_2$. If mercurous chloride is treated with a solution of ammonia, it turns black and produces an insoluble compound which has the formula $N\,H_2\,Hg_2\,Cl$:

$$2\,Hg\,Cl + 2\,N\,H_3 = N\,H_2\,Hg_2\,Cl + N\,H_4\,Cl;$$

this substance is regarded as being ammonium chloride in which two atoms of hydrogen have been replaced by mercury:*



$$N\left\{\begin{array}{l}H\\H\\H\\H\\Cl\end{array}\right. \text{ ammonium chloride, and } N\left\{\begin{array}{l}H\\H\\Hg\\Hg\\Cl\end{array}\right. \text{ mercurous chloramide.}$$

If mercurous chloride is boiled with hydrochloric acid it is converted into mercuric chloride and mercury:

$$2\,Hg\,Cl = Hg + Hg\,Cl_2.$$

Sulphuric acid, hot and concentrated, changes it into a mixture of mercuric sulphate and mercuric chloride, nitric acid into mercuric nitrate and mercuric chloride. Chlorine readily converts calomel into mercuric chloride.

Mercuric chloride.—This salt can be produced either by heating mercury in a current of chlorine,† by dissolving the metal in aqua regia, or by dissolving mercuric oxide in hydrochloric acid. The corrosive sublimate of commerce is usually prepared by heating mercuric sulphate with sodium chloride in wide-mouthed retorts; the mercuric chloride sublimes and collects on the cold portions of the vessel, while sodium sulphate remains behind:

$$Hg\,S\,O_4 + 2\,Na\,Cl = Hg\,Cl_2 + Na_2\,S\,O_4.$$

Corrosive sublimate is a transparent, crystalline mass which is soluble in water and which crystallizes from that solvent when evaporated; it crystallizes from aqueous solution in thin prisms; one hundred parts of water at 0° dissolve 5.73 parts, and at ordinary temperatures about 7 parts of mercuric chloride. The solutions the red variety by sublimation. Black mercuric sulphide is also produced by rubbing mercury and sulphur together. Mercuric sulphide is not attacked by dilute acids; concentrated nitric acid in part dissolves it and in part converts it into a white, insoluble double compound of mercuric nitrate and mercuric sulphide; this compound has the formula $Hg(NO_3)_2 2 HgS$. Cimabar when heated turns black, and unless the temperature was too high resumes its original red color on cooling.

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* It will be remembered that the same power of replacing hydrogen in ammonium chloride is found in the case of *cuprous chloride;* the formula of this ammonium compound is, however, $Cu\,Cl, N\,H_3$ or $N\,H_3\,Cu\,Cl$. Argentic chloride, $Ag\,Cl$, also possesses the power of absorbing ammonia.

† The mercury burns with a pale flame and forms a white sublimate of mercuric chloride.

All mercury compounds, if they are salts of volatile acids, are volatile; if, on the other hand, they are salts of not-volatile acids, either the acids themselves or their decomposition products remain after heating (see page 184).

TYPICAL COMPOUNDS IN THIS FAMILY.

	Oxides.	Hydroxides.	Chlorides.	Sulphates.	Sulphides.
Zinc	ZnO	$Zn(OH)^2$†	$ZnCl_2$ ‡	$ZnSO_4 + 7 H_2O$	ZnS**
Cadmium	CdO	$Cd(OH)^2$	$CaCl_2$ ‡	$3 CdSO_4 + 8 H_2O$	CdS
Mercury	HgO*	———	$HgCl_2$ §	$HgSO_4$	HgS

* Exists in two varieties, yellow and red.

† Both basic and acidic in its character: $Zn(OH)_2 + 2 HCl = ZnCl_2 + 2 H_2O$ and $Zn(OH)_2 + 2 KOH = Zn(OK)_2 + 2 H_2O$.

‡ Readily form double chlorides with ammonium chloride. The latter are not decomposed by ammonia.

§ Forms mercuric chloramide, NH_2HgCl, with ammonia.

** Soluble in dilute acids.

All of the salts of the elements belonging to this group show a great tendency to produce double salts.

MERCUROUS COMPOUNDS (not typical).

Hg_2O, mercurous oxide.

$HgCl$, mercurous chloride.

$HgNO_3$, mercurous nitrate.

Mercurous chloride is insoluble in water. When covered with ammonia solution it forms mercurous chloramide. NH_2Hg_2Cl, the nitrate forms basic salts on addition of water.

CHAPTER LVI.

THE ELEMENTS BELONGING TO THE PRIMARY GROUPS OF THE FAMILIES III, IV AND V, OF THE LONG PERIODS.

The elements comprising the primary group of the third family bear somewhat the same relation to boron and aluminium that calcium strontium and barium do to beryllium and magnesium. The elements are:

Scandium, symbol Sc, atomic weight 44.
Yttrium, symbol Y, “ “ 89.1.
Lanthanum, symbol La, “ “ 138.2.
Ytterbium, symbol Yb, “ “ 173.

All of these elements are extremely rare, they occur in an orthosilicate known as gadolinite, the most common formula of which is $Be_2 (YO)_2 Fe (Si O_4)_2$, and also in an extremely complicated salt of titanic acid known as euxenite. Considerable uncertainty has existed as to the number of elements really contained in this and in the following group, for some investigators, by reason of the peculiarities of the absorption spectra of some of the salts of these metals, have undertaken to prove that the usually accepted number must be largely increased.

Scandium, it will be remembered, was one of the elements predicted by Mendelejeff (see page 357). The typical oxide of these elements is $M_2 O_3$, corresponding to $B_2 O_3$ and $Al_2 O_3$, this oxide is basic in its character, it does not dissolve in caustic alkalis, so that these elements are more metallic than is aluminium. The hydroxides have the formula $M (OH)_3$, the sulphates, $M_2 (SO_4)_3$ and, *unlike the sulphates of the secondary group of this family**, they do not form alums; this distinction is similar to that existing between the sulphates of calcium, strontium and barium and those of zinc, cadmium and mercury, for the sulphates of the first three are insoluble, while those of the second three are soluble and have a great tendency to form double salts with the sulphates of the alkalis.

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* Sulphates of aluminium, gallium, indium, thallium.

The elements comprising the primary group of family IV are:

Titanium, symbol Ti, atomic weight, 48.
Zirconium, symbol Zr, " " 90.6.
Cerium, symbol Ce, " " 140.2.
Thorium, symbol Th, " " 232.6.

Of the compounds of these four elements, those of titanium are by far the most common, indeed compounds containing titanium are not at all infrequent, for the element occurs in many iron ores; titanic iron ore is looked upon as being ferrous titanate, $Fe\,Ti\,O_3$, the compound is, however, isomorphous with ferric oxide and frequently occurs in company with that extremely important substance; furthermore, titanic oxide is often a constituent of magnetic iron ore, $Fe_3\,O_4$, which latter substance is a member of the spinell group (see page 326), so that it seems not improbable that titanic iron is really derived from a hydroxide $Ti\,O\,(O\,H)$, which is analgous to $Al\,O\,(O\,H)$, if this relationship is granted, then titanium can, under certain circumstances, act as a trivalent element, and this behavior would bring it in line with cerium (see below). Titanium dioxide $Ti\,O_2$ is found in two mineral forms, brookite and anatas,[*] and as a polymeric form $Ti_2\,O_4$, which is called rutile, and which is isomorphous with a silicate of zirconium, $Zr\,Si\,O_4$, known as zircon, and with tin stone (see page 305). The relationship between these three oxides, which all belong to elements in the same family, and which are isomorphous, becomes apparent if we double the formula of the oxide of tin, thus:

$Sn\,Sn\,O_4$, tin stone,
$Ti\,Ti\,O_4$, rutile,
$Zr\,Si\,O_4$, zircon.

The compounds of the elements of this group are analogous to those of silicon, this connection will be seen from the following:

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[*] These two oxides of titanium are not isomorphous with quartz and tridymite, yet the form of brookite is so close to that of tridymite that isomorphism is considered possible (Groth). (See page 293).

	Oxides.	Chlorides.	Fluorides.	Hydroxides.	Metahydroxides.
Silicon,	$Si\,O_2$	$Si\,Cl_4$*	$Si\,F_4$**	$Si\,(OH)_4$	$Si\,O_3\,H_2$
Titanium.	$Ti\,O_2$	$Ti\,Cl_4$*	$Ti\,F_4$**	$Ti\,(OH_4)$	$Ti\,O_3\,H_2$ (?)
Zirconium,	$Zr\,O_2$	$Zr\,Cl_4$†	$Zr\,F_4$**	$Zr\,(OH)_4$	....
Thorium.	$Th\,O_2$	$Th\,Cl_4$††	$Th\,F_4$**	$Th\,(OH)_4$	....

* Decomposed by water.

† Partially decomposed by water; forming a basic chloride:

$$Zr\left\{\begin{matrix}Cl + HOH\\ Cl + HOH\\ Cl\\ Cl\end{matrix}\right. = Zr\left\{\begin{matrix}OH\\ OH\\ Cl\\ Cl\end{matrix}\right. + 2\,H\,Cl;\ Zr\left\{\begin{matrix}OH\\ OH\\ Cl\\ Cl\end{matrix}\right. = Zr\left\{\begin{matrix}O\\ Cl\\ Cl\end{matrix}\right. + H_2\,O.$$

†† Not decomposed except by hot water.

** All of these fluorides behave exactly as does silicon tetrafluoride; they form compounds analogous to fluosilicic acid and the fluosilicates, (see page 291).

$H_2\,Si\,F_6$, fluosilicic acid; $K_2\,Si\,F_6$, potassium fluosilicate.
$H_2\,Ti\,F_6$, fluotitanic acid: $K_2\,Ti\,F_6$, potassium fluotitanate.
$K_2\,Zr\,F_6$, potassium fluozirconate.
$K_2\,Th\,F_2$, potassium fluothorate.

The above table and the following foot notes very plainly show the intimate family connection between silicon and the three following elements; the oxides of titanium and zirconium resemble silicon dioxide in the fact that, after they have been heated, they are insoluble in water and even in the strongest acids or alkalis, to be brought in solution they must be heated with concentrated sulphuric acid for a long time, or they must be fused with alkalis, the oxide of thorium is somewhat less obstinate. The three last elements in the above table, having higher atomic weights than silicon, are also more metallic in their nature, their hydroxides are consequently both weak acids and weak bases. The salts in which they act as acids are but little known, indeed, it is doubtful if thorium hydroxide has acid properties. The alkali salts, so far as known, correspond to the metasilicates, and hence have the general formula $M_2\,XO_3$. Among the salts derived from the hydroxides acting as bases the sulphates, with the general formula $M\,(SO_4)_2$ are perhaps the most prominent. The chemistry of cerium is, as yet, uncertain in many respects; the element forms two series of compounds, in one of which, presenting compounds such as $Ce_2\,O_3$, $Ce\,Cl_3$, $Ce\,(NO_3)_3$, it is trivalent, and resembles lanthanum, an element in the preceding family, in the other it is tetravalent and by means of compounds $Ce\,F_4$, $Ce\,O_2$, $Ce\,(SO_4)_2$ it falls in line with the family numbered

IV. It may be added that titanium likewise forms more than one oxide, for a compound $Ti_2 O_3$ and a sulphate $Ti_2 (SO_4)_3$ have been described.

The elements comprising the primary group of family V are:

Vanadium,	atomic	weight,	51.4	symbol	V.
Columbium,	"	"	94.	"	Cb.
Didymium,	"	"	142.3	"	Di.
Tantalum,	"	"	182.6	"	Ta.

Although more metallic in their nature than the elements forming the secondary group of this family,[*] the four elements, with perhaps the exception of didymium, bear many points of resemblance to the latter; didymium, indeed, has lately been separated into two elements, neodidymium and praseodidymium, in some respects these two substances are very much like cerium and lanthanum, being trivalent in most of their compounds. Vanadium is the best known of all of these elements. This element is as much like arsenic or antimony as titanium is like silicon, in very many respects it is, indeed, like the typical element of the family, nitrogen, for it forms as many oxides as the latter, and these oxides have similar formulæ, thus:

Oxides of nitrogen.	Oxides of vanadium.
$N_2 O$	$V_2 O$
$N O (N_2 O_2)$	$V_2 O_2$
$N_2 O_3$	$V_2 O_3$
$N O_2$, $N_2 O_4$	$V_2 O_4$
$N_2 O_5$	$V_2 O_5$

Vanadium occurs in nature chiefly as the lead, zinc or bismuth salts of vanadic acid. Vanadinite is a double salt composed of lead vanadate and lead chloride having the formula $3 Pb_3 (V O_4)_2 + PbCl_2$.[†] The element forms three chlorides, $V Cl_2$, $V Cl_3$ and $V Cl_4$. The most important compounds of vanadium are the vanadic acids, which correspond to those of phosphorus and arsenic, the latter being elements belonging to the same family:

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[*] Arsenic, antimony and bismuth.

[†] Vanadinite is isomorphous with apatite which has a formula $3 Ca_3 (P O_4)_2 +$ $Ca Cl_2$, calcium replacing lead and vanadium *replacing phosphorous isomorphously.*

	Oxides.	Meta-acids.	Ortho-acids.	Pyro-acids.
Phosphorus	P_2O_5	HPO_3	H_3PO_4	$H_4P_2O_7$
Arsenic	As_2O_5	$HAsO_3$	H_3AsO_4	$H_4As_2O_7$
Vanadium	V_2O_5	HVO_3	H_3VO_4	$H_4V_2O_7$

Vanadates of all these acids are known, for instance we have:

$Na VO_3$,	sodium	metavanadate.
$Na_3 VO_4$,	"	orthovanadate.
$Na_4 V_2 O_7$	"	pyrovanadate.

In addition to the above, however, more complicated salts of polyvanadic acids, which are formed in the same manner as the polysilicic acids, are known. Free metavanadic acid is a golden-yellow, crystalline compound. Reducing agents readily change vanadic acid into the lower acid, V_2O_4.

Columbium and tantalum are very rare elements which differ from vanadium just as much as antimony does from arsenic, for they are able to form pentachlorides and pentabromides while the pentahalides of vanadium have not as yet been prepared. Columbium is also frequently termed niobium. It occurs in the mineral columbite, which is a metacolumbate of iron, having the formula $Fe (Cb O_3)_2$, tantalum is found as a metatantalate of iron, $Fe (Ta O_3)_2$.

The brief mention of the very rare metals which have been discussed in this chapter is sufficient to demonstrate the family relationship existing between them and the much more common elements which were described in the first portion of the book, of course they form a great number of compounds, some of them very complicated, which cannot be taken up in a book of this kind; for this study a large manual must be consulted.

CHAPTER LVII.

THE ELEMENTS BELONGING TO THE PRIMARY GROUP OF THE SIXTH FAMILY.

Chromium, symbol Cr; atomic weight, 52.1; Molybdenum, symbol Mo; atomic weight, 96; Tungsten (Wolfram) symbol W; atomic weight, 184; Uranium, symbol U; atomic weight, 239.6.

The typical elements belonging to the sixth family, in the short periods, are oxygen and sulphur and, as has been shown by the arrangement of the periodic system given on page 355, the individuals more immediately connected with those two elements are selenium and tellurium, while chromium, molybdenum, tungsten and uranium, having their positions near the middle of the long periods, vary much more from the character of the types in the short periods than the metals which have been discussed in the preceding chapters do. The metallic nature of the elements forming the primary group of the sixth family is most apparent in the behavior of the lower oxides and in the salts derived from these; the highest oxide of each element is the typical one, XO_3; this compound displays the character of an acidic anhydride although, in the case of the most metallic element of the family, namely uranium, it is also basic under some circumstances. The salts derived from the typical oxide, in formula, correspond to the sulphates, selenates and tellurates, and in some instances to the pyrosulphates (see page 150); this relationship is made apparent by the following table:

Oxides.	Acids.	Salts.	Pyro-salts.	Oxides.	Acids.	Salts.	Di-Salts.
SO_3	H_2SO_4	M_2SO_3	$M_2S_2O_7$	CrO_3	H_2CrO_4[*]	M_2CrO_4	$M_2Cr_2O_7$
(SeO_3)	H_2SeO_4	M_2SeO_3		MoO_3	H_2MoO_4[†]	M_2MoO_4	$M_2Mo_2O_7$
TeO_3	H_2TeO_4	M_2TeO_3		WO_3	H_2WO_4[†]	M_2WO_4	$M_2W_2O_7$
				UO_3			$M_2U_2O_7$

[*] The acid is not known, when liberated from its salts it breaks down into its anhydride, CrO_3, and water.

[†] The ortho acid, H_4XO_6 is also known.

Chromium, molybdenum and tungsten further form a number of very complicated salts derived from poly-acids which are produced in a manner analogous to the polysilicates, (see page [illegible]).

The most marked characteristic of these elements, and this they share with the others having their position at the middle of the long periods, lies in the power which the individuals possess of forming several series of compounds in each of which they exhibit a different valence; so, for instance, molybdenum forms the chlorides $Mo\,Cl_2$, $Mo\,Cl_3$, $Mo\,Cl_4$ and $Mo\,Cl_5$, while tungsten exhibits $W\,Cl_2$, $W\,Cl_4$, $W\,Cl_5$ and $W\,Cl_6$, these two elements possess chlorides, therefore, in which they are respectively quinquivalent and hexavalent, and, passing backward from these, we find a series of compounds in which the valence successively diminishes by one until a minimum is reached at divalence. It will be remembered that sulphur shows some resemblance to molybdenum and tungsten by forming three chlorides of the formulæ $S_2\,Cl_2$, $S\,Cl_2$ and $S\,Cl_4$ respectively, but the latter is only capable of existence at very low temperatures; it is not inconceivable therefore that, were the proper conditions attainable, a penta and hexa chloride of sulphur might also be produced (see page 354).

None of the elements of this group occur uncombined as natural minerals, the principal compounds which are found are given on the following table:

Chromium:—Found as chromite (chromic iron) isomorphous with spinell, formula $Fe\,(Cr\,O_2)_2$,* when the chromium is replaced in part by aluminium and by ferric iron, and the ferrous iron by magnesinm, the mineral is called chromspinell; chromite forms veins or imbedded masses in serpentine rock.

Crocoite:—Lead chromate, $Pb\,Cr\,O_4$,† is sometimes found.

Molybdenum:—Found as the sulphide, $Mo\,S_2$, called molybdenite; as the molybdate of lead, $Pb\,Mo\,O_4$, called wulfenite ‡ and as molybdite, $Mo\,O_3$, the anhydride of molybdic acid.

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* This compound is ferrous chromite, derived from a hydroxide of the formula $Cr\,O\,(O\,H)$, analogous to $Al\,O\,(O\,H)$. The ferrous iron in chromite can be replaced isomorphously by divalent chromium, the trivalent chromium $Cr\,O\,(O\,H)$ by ferric iron (see page 326).

† The chromates of the alkali metals are, without exception, isomorphous with the corresponding sulphates; naturally occurring lead chromate is, however, *not* isomorphous with anglesite ($Pb\,S\,O_4$) but artificially prepared crystals of lead chromate have proven to be isomorphous with the latter. The isomorphism of the chromates and sulphates clearly demonstrates the family connection between chromium and sulphur.

‡ Wulfenite is not isomorphous with crocoite but it is sometimes found with a contents of chromium replacing molybdenum. It *is* isomorphous with the corresponding salt of tungstic acid.

Tungsten.—As scheelite, $Ca\,W\,O_4$; reinite, $Fe\,W\,O_4$, and stoltzite, $Pb\,W\,O_4$. All of these minerals are isomorphous with wulfenite. Tungsten is also found as tungstite, $W\,O_3$, the anhydride of tungstic acid.

Uranium.—As pitchblende, $(U\,O_2, Pb)\,W_2\,O_9$, and as the sulphate of uranium, which exists as an impure mineral sometimes called uranocher.

The elements under discussion are not of any commercial importance when isolated from their compounds. *Chromium* can be prepared by electrolyzing the fused chloride, $Cr\,Cl_3$, in a manner analogous to the preparation of the alkali metals, the alkaline earths and of aluminium, or the metal can be obtained by heating the chloride with sodium or with zinc in the absence of the air, the process being like that formerly used for obtaining aluminium (see page 321). Sodium amalgam, when treated with chromic chloride, forms sodium chloride and liberates chromium, which latter element then forms an amalgam with mercury. It can be separated from this by distilling the mercury in a current of hydrogen. *Tungsten, molybdenum and uranium* can be prepared by reducing the oxides of these metals by means of hydrogen at red heat, the elements in question being much more easily separated from their oxides than is chromium from its corresponding compounds. In the case of uranium the element can even be obtained by heating its oxides with charcoal. The most important physical properties of these elements are given in the following table:

Chromium, specific gravity 6.8, crystalline, of metallic appearance, infusible.
Molybdenum, specific gravity 8.6, silver white, infusible.
Tungsten, specific gravity 18.1, steel-colored plates, fusible at a high temperature.
Uranium, specific gravity 18.4, white, metallic lustre, fusible at a high temperature.

Chromium, molybdenum, tungsten and uranium all have small atomic volumes. ~~As was mentioned on~~ page 352, they have their places on the descending branches and near the minimum of the curves formed by using the atomic volumes as ordinates and the atomic weights as abscissæ; they are therefore infusible, or at least fusible with difficulty, and they form colored salts.

Chromium is slowly oxidized when heated in the air, more rapidly in a current of oxygen; the oxide which is formed has the formula $Cr_2\,O_3$. The metal is dissolved by hydrochloric acid or by hot sulphuric acid, the chloride $Cr\,Cl_3$ or the sulphate $Cr_2\,(S\,O_4)_3$ being produced according to the acid used. Potassium nitrate or potassium chlorate, when fused with chromium, give up their oxygen and form potassium chromate.

Molybdenum is slowly attacked when heated in the air. It is readily converted into the trioxide, $Mo\,O_3$, by oxygen at a high temperature. Nitric acid or aqua regia attack the metal to form molybdic acid. *Tungsten* behaves as does molybdenum, while *uranium* even dissolves in dilute hydrochloric or sulphuric acid, hydrogen being at the same time evolved.

The most important compounds of chromium are derived from two oxides, *chromic oxide*, $Cr_2\,O_3$, which is mainly basic in its character, and *chromium trioxide*, $Cr\,O_3$, which acts as an acidic anhydride and which is the oxide typical of the family. In addition to these two there exists a *chromous hydroxide*, $Cr\,(O\,H)_2$, (the oxide corresponding to which is not known) and a chromous-chromic oxide of the formula $Cr_3\,O_4$.

Chromic oxide, $Cr_2\,O_3$, is a dark green powder which is insoluble in acids after it has been heated to a high temperature (see page 326); after it has been subjected to such treatment it can be brought into solution by fusion with caustic alkalis or with the primary sulphate of potassium.* Chromic oxide dissolves in fused glass and imparts a fine green color to the substance; for this reason it is used as a green paint for tinting porcelain.

Chromic hydroxide can be precipitated from solutions of chromic salts by the addition of ammonia water. When dry it has the composition represented by the formula $Cr\,(O\,H)_3 + 2\,H_2\,O$. When the latter is heated to 200° it changes to metachromic hydroxide, $Cr\,O\,(O\,H)$. This substance corresponds to the similar aluminium compound (see page 326). Chromic oxide and hydroxide are both basic and acidic in their character. The freshly precipitated hydroxide is readily dissolved by caustic alkalis, forming deep green solutions of the *chromites* of the respective metals; if the solutions so formed are allowed to stand, or if they are boiled, the hydroxide is once more precipitated.† A number of chromites occur as minerals;

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* In this process potassium-chrom alum, $K_2\,S\,O_4, Cr_2\,(S\,O_4)_3 + 24\,H_2\,O$, is produced.

† Difference from aluminium hydroxide, the solution of the latter in alkalis is not decomposed by boiling. When chromic oxide is present, alkalis are also able to dissolve considerable quantities of ferric oxide.

the latter are derived from metachromic hydroxide and are isomorphous with spinell; these compounds can also be artificially prepared by fusing chromic oxide with the metallic oxide which is to be used as the base, boron trioxide, B_2O_3, being used as a flux.[*] The *chromic salts*, in which chromic oxide acts as a base, are produced by dissolving the oxide or hydroxide in acids. The most important of these are described below:

Chromic chloride, $CrCl_3$[†] is produced by burning chromium in an atmosphere of chlorine or by heating an intimate mixture of chromic oxide and charcoal in a current of dry chlorine; the salt so produced sublimes in the form of pink plates; the chloride which is formed by dissolving the hydroxide in water crystallizes in dark green needles of the formula $CrCl_3 + 6\,H_2O$, anhydrous chromic chloride cannot be prepared from this, as, upon heating, the salt loses hydrochloric acid and changes into a basic chromic chloride. The dry chloride is nearly insoluble in water or in acids; when heated in air it gives off chlorine and leaves chromic oxide.

Chromic sulphate, $Cr_2(SO_4)_3 + 15\,H_2O$ is formed by dissolving chromic hydroxide is concentrated sulphuric acid and then allowing the solution to absorb moisture from the air; the salt is reddish violet in color, when heated to 100° it loses water of crystallization and changes to a green salt having the composition $Cr_2(SO_4)_3 + 5\,H_2O$. When a solution of chromic sulphate is mixed with a solution of an alkaline sulphate and evaporated, an alum is formed in which chromium has taken the place of aluminium, an example of such a salt is $K_2SO_4, Cr_2(SO_4)_3 + 24\,H_2O$, (see page 327).

When solutions of caustic-alkalis are added to solutions of chromic salts, a precipitate of chromic hydroxide is produced, the latter is soluble in an excess of the precipitating medium; on the other hand chromic hydroxide does not dissolve in ammonia solution and can, as a consequence, be precipitated from solutions of chromic salts by the addition of that reagent, even in excess;[‡] alkaline sulphide solutions or solutions of the carbonates precipitate chromic hydroxide for reasons identical with those mentioned in the chapter on aluminium, (see page 329)*. When in alkaline solution, chromic hydroxide is completely oxidized to a *chromate* by the addition of chlorine or bromine, the same change can also be brought about by the addition of other oxidizing agents † or by fusion with potassium nitrate or chlorate.

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[*] Zinc chromite, $Zn(CrO_2)_2$, and manganous chromite, $Mn(CrO_2)_2$ have been prepared in this way.

[†] The formula Cr_2Cl_6 was formerly assigned to this compound, but the latest determinations of the specific gravity of this substance, while in the state of a vapor, show it to be $CrCl_3$, (see page 323).

[‡] The precipitation of chromic hydroxide is very much retarded and may be entirely prevented by the presence of not-volatile organic acids such as citric acid, tartaric acid, oxalic acid, etc.

Chromic acid, $H_2 Cr O_4$, is not known, its anhydride, $Cr O_3$, *chromium trioxide*, is produced when the acid is liberated from its salts, this is best accomplished by adding tolerably concentrated sulphuric acid to a solution of potassium or sodium dichromate:

$$K_2 Cr_2 O_7 + H_2 SO_4 = K_2 SO_4 + H_2 O + 2 Cr O_3.$$

The anhydride crystallizes in beautiful carmine-red needles which melt at 193°, forming a dark red fluid which loses oxygen at 250° and changes to green chromic oxide; the oxide is readily soluble in water, the solubility being diminished by the addition of sulphuric acid.‡

Chromium trioxide is a most energetic oxidizing agent, even dilute solutions instantly change sulphurous acid into sulphuric acid:

$$1.\quad 2 Cr O_3 + 3 H_2 SO_3 = Cr_2 O_3 + 3 H_2 SO_4;$$
$$2.\quad Cr_2 O_3 + 3 H_2 SO_4 = Cr_2 (SO_4)_3 + 3 H_2 O;$$

in the same way hydrogen sulphide is oxidized, while sulphur is separated. Many organic substances are also readily attacked by chromium trioxide,§ that substance being at the same time reduced to chromic oxide (respectively to the chromic salts which would be formed by the acids which may be present).

Although chromic acid is unknown, an *acid chloride of chromium* called *chromylchloride*, $Cr O_2 Cl_2$, which may be considered as being chromic acid in which the two hydroxyle groups have been replaced by chlorine, can be produced by adding concentrated sulphuric acid

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[*] Chromium is completely separated from solutions of chromic salts by the addition of freshly precipitated barium carbonate. The chromium separates as chromic hydroxide mixed with basic chromic salt.

[†] For instance lead superoxide, $Pb O_2$, when lead chromate is produced.

[‡] Chromium trioxide is least soluble in sulphuric acid of about 85 per cent.

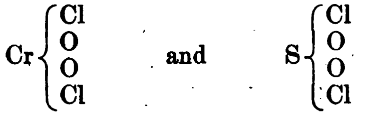
[§] For instance, alcohol is oxidized to aldehyde and to acetic acid, the relationship between these three compounds can be seen from the following structural formulæ:

$$\underset{\text{alcohol,}}{CH_3 - CH_2\ OH} + O = \underset{\text{aldehyde,}}{CH_3 - COH} + O = \underset{\text{acetic acid.}}{CH_3 - CO\ OH.}$$

to a mixture of sodium chloride and potassium dichromate. Chromylchloride is a dark red fluid which boils at 118° and which instantly decomposes into chromium trioxide and hydrochloric acid on the addition of water:

$$Cr\,O_2\,Cl_2 + H_2\,O = 2\,H\,Cl + Cr\,O_3.$$

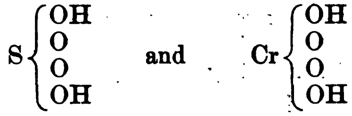
In structure this compound is analogous to sulphurylchloride:



$$Cr\left\{\begin{matrix}Cl\\O\\O\\Cl\end{matrix}\right. \quad \text{and} \quad S\left\{\begin{matrix}Cl\\O\\O\\Cl\end{matrix}\right.$$

Chromylchloride and Sulphurylchloride (see page 152).

The chromates are derived from a hypothetical dibasic acid analogous in formula to sulphuric acid:



$$S\left\{\begin{matrix}OH\\O\\O\\OH\end{matrix}\right. \quad \text{and} \quad Cr\left\{\begin{matrix}OH\\O\\O\\OH\end{matrix}\right.$$

Sulphuric acid and chromic acid,

and the dichromates form a dichromic acid, $H_2\,Cr_2\,O_7$ (also hypothetical), which is analogous to disulphuric acid, $H_2\,S_2\,O_7$ (see page 150).[*] The most important chromates and dichromates are those of potassium and sodium.

Potassium chromate is a yellow, crystalline salt, which is readily soluble in water and which is isomorphous with potassium sulphate. Upon addition of dilute acids it is converted into the dichromate: $2\,K_2\,Cr\,O_4 + 2\,H\,N\,O_3 = K_2\,Cr_2\,O_7 + 2\,K\,N\,O_3 + H_2\,O$.[†] On the other hand, potassium *dichromate* is changed to the *chromate* by alkalis, thus: $K_2\,Cr_2\,O_7 + 2\,K\,O\,H = 2\,K_2\,Cr\,O_4 + H_2\,O$.

Potassium dichromate crystallizes in large, red plates which are soluble in water. When heated it melts without decomposition. At a high temperature, however, it loses oxygen and is converted into a mixture of chromic oxide and potassium chromate:

$$2\,K_2\,Cr_2\,O_7 = 2\,K_2\,Cr\,O_4 + Cr_2\,O_3 + 3\,O.$$

A similar loss of oxygen takes place when the salt is heated

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[*] Tri and polychlorates have also been described (see page 296).

[†] In this reaction the *primary* chromate of potassium, $K\,H\,Cr\,O_4$ may be considered to be the first product:

$$K_2\,Cr\,O_4 + H\,N\,O_3 = K\,H\,Cr\,O_4 + K\,N\,O_3.$$

Two formula weights of this primary salt would then separate water between them, leaving the dichromate:

$$2\,K\,H\,Cr\,O_4 = K_2\,Cr_2\,O_7 + H_2\,O.$$

with sulphuric acid. In the latter case chromic sulphate (respectively potassium chrome alum) is formed:

$$K_2Cr_2O_7 + 4\,H_2SO_4 = K_2SO_4, Cr_2(SO_4)_3 + 4\,H_2O + 3\,O.^*$$

Potassium dichromate is extensively used for the preparation of battery fluids; however, of late years, the more soluble sodium dichromate is taking the place of the former salt.

The reactions shown by sodium dichromate are identical with those of potassium dichromate.

The chromate of lead is insoluble in water and is produced by adding a soluble chromate or dichromate to the solution of a lead salt, as follows:

1. $K_2CrO_4 + Pb(NO_3)_2 = 2\,KNO_3 + PbCrO_4$.
2. $K_2Cr_2O_7 + 2\,Pb(NO_3)_2 + H_2O = 2\,KNO_3 + 2\,HNO_3 + 2\,PbCrO_4$.

In the second reaction, therefore, free acid is produced; the same is true in other cases where, by double decomposition, an insoluble chromate can be formed, for the precipitation takes place by the addition of either a soluble chromate or *dichromate* to the solution containing the salt of the metal capable of forming such an insoluble chromate. Lead chromate possesses a bright yellow color which makes it useful as a paint, the name of which is *chrome yellow;* addition of potassium or sodium hydroxide to chrome yellow changes that substance into an insoluble basic lead chromate which is termed *chrome red:*

$$2\,PbCrO_4 + 2\,KOH = (PbOH)_2CrO_4 + K_2CrO_4.$$

Barium chromate, $BaCrO_4$, is insoluble in water, but soluble in hydrochloric or nitric acid. In this way the salt differs from the equally insoluble barium sulphate, for the latter is insoluble both in water and in acids.

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* In this reaction the oxygen present in the chromate, in excess of that necessary to form chromic oxide, passes off. The same is true of the other reactions in which potassium dichromate, or dichromates in general, are used as oxidizing agents. *One formula weight of potassium dichromate,* therefore, has *three atoms of oxygen* at its disposal for oxidizing purposes. In formulating reactions this fact is the essential one to be taken into consideration. One formula weight of potassium dichromate will therefore oxidize *three* of sulphurous acid to sulphuric acid, or *three* molecules of alcohol to aldehyde, etc. Concentrated hydrochloric acid is oxidized to chlorine by the dichromate; in the latter case, of course, *six* molecules of hydrochloric acid are changed to chlorine by the dichromate, for:

$$6\,HCl + 3\,O = 3\,H_2O + 6\,Cl;$$

however the excess of hydrochloric acid will subsequently form potassium chloride and chromic chloride with the bases present, so that the complete reaction would be represented as follows:

$$K_2Cr_2O_7 + 14\,HCl = 2\,KCl + 2\,CrCl_3 + 6\,Cl + 7\,H_2O.$$

The *chromous compounds* which are derived from chromous hydroxide, $(Cr\,O\,H)_2$, are of far less importance than either the chromic salts or the chromates.

Chromous chloride, $Cr\,Cl_2$, is produced when metallic chromium is dissolved in hydrochloric acid or when chromic chloride, $Cr\,Cl_3$, is reduced by means of a current of hydrogen. The substance produces a blue solution in water; the latter, however, rapidly turns green, owing to the absorption of oxygen and the formation of a basic chromic chloride. In fact, the chief characteristic of all *chromous* compounds is the extreme ease with which they take up oxygen in order to produce chromic salts.

An oxide of chromium having the formula $Cr_3\,O_4$ is also known. This substance is regarded as being composed of chromous and chromic oxides.

$$Cr\,O + Cr_2\,O_3 = Cr_3\,O_4;$$

so that, in this compound, chromous oxide plays the part of a base and chromic oxide that of an acidic anhydride.

The compounds of chromium which are used in the arts are prepared from chromic iron. The latter substance is finely ground, intimately mixed with potash-lime* and then heated in furnaces in which a free circulation of air is provided for, the oxygen so supplied changing the chromic compound into potassium chromate and calcium chromate;† after heating for a sufficient length of time, the mass is extracted with a solution of potassium sulphate, by which means all of the calcium chromate is converted into potassium chromate and the latter salt is finally changed to potassium dichromate by the addition of sulphuric acid. Potassium and sodium dichromates are used for the preparation of various paints, (chrome yellow, chrome red, etc.), in a number of processes of dyeing, in the preparation of chromic oxide, which is used for porcelain painting, as oxidizing agents and in a number of other ways.

The compounds of molybdenum, tungsten and uranium are not by any means so important as are those of chromium.

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*A mixture of potassium and calcium hydroxides produced by slaking quicklimd with a potassium hydroxide solution, soda-lime is produced by using sodium instead of potassium hydroxide.

†Of course, in the preparation of sodium dichromate, soda-lime is used.

Molybdenum forms the following oxides:

1. Molybdenum trioxide, $Mo O_3$; white in color;
2. Molybdic oxide, $Mo_2 O_3$; black in color;
3. Molybdenum dioxide, $Mo O_2$; dark brown in color.‡
4. Molybdenum monoxide, MO black brown in color.

The first of these is produced by roasting the mineral molybdenite, by which means the sulphur is burned off and molybdenum trioxide is left, the latter is extracted with ammonia water, which latter produces ammonium molybdate; pure molybdic acid is separated from the salt by the addition of nitric acid:

$$(N H_4)_2 Mo O_4 + 2 H N O_3 = 2 N H_4 N O_3 + H_2 O + H_2 Mo O_4.$$

The trioxide is produced by dehydrating the latter compound. The oxide is difficultly soluble in water, is white and of crystalline structure; reducing agents, such as sodium amalgam, reduce it to the second oxide, $Mo_2 O_3$, and this, when gently heated, takes up oxygen and forms the dioxide, $Mo O_2$; the fourth oxide is formed by adding a hot solution of potassium hydroxide to molybdenum dichloride, $Mo Cl_2$. Hydroxides, $Mo (O H)_3$ and $Mo (O H)_4$, corresponding to $Mo_2 O_3$ and $M O_2$ are also known.

Molybdenum forms the following chlorides:

$Mo Cl_5$, produced by passing chlorine over heated molybdenum.
$Mo Cl_4$, produced by heating the trichloride.*
$Mo Cl_3$, produced by heating the pentachloride in a current of hydrogen at 250°.
$Mo Cl_2$, produced by heating the trichloride in a current of carbon dioxide.*

Molybdenum pentachloride boils at 268°, changing into a dark brown gas which has a specific gravity of 9.4 at 350°; this vapor density corresponds to a molecule having the formula $Mo Cl_5$, so that molybdenum affords an example of an element belonging to the sulphur family which enters into the formation of a compound in which the individual is pentavalent (see page 354).

Unlike chromium trioxide, the trioxide of molybdenum is capable of forming a number of hydrated acids which in formula correspond to the hydrated sulphuric acids; this relationship is made plain by the following table:

MOLYBDIC ACIDS.	SULPHURIC ACIDS (see page 147).
$Mo O_3 + H_2 O = H_2 Mo O_4$.	$S O_3 + H_2 O = H_2 S O_4$.
$H_2 Mo O_4 + H_2 O = H_4 Mo O_5$.	$H_2 S O_4 + H_2 O = H_4 S O_5$.
$H_4 Mo O_5 + H_2 O = H_6 Mo O_6$.	$H_4 S O_5 + H_2 O = H_6 S O_6$.

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‡ A blue oxide, $Mn_3 O_8$, is also described.

* $2 Mo Cl_3 = Mo Cl_2 + Mo Cl_4$.

The acid having the formula $H_4 Mo O_5$ is formed by adding nitric acid to a solution of sodium or potassium molybdate. It is nearly insoluble in water and in drying in vacuo loses water while changing to $H_2 Mo O_4$. $H_6 Mo O_6$ is soluble in water and is produced by dialysis of a solution of molybdic acid in a manner similar to the separation of soluble silicic acid (see page 294). Salts of a number of complicated molybdic acids are also known; the formulæ of a few of these are given in the following table:

$Na_2 Mo_2 O_7$, sodium dimolybdate.*
$Na_2 Mo_3 O_{10}$, sodium trimolybdate.
$Na_2 Mo_4 O_{13}$, sodium tetramolybdate.
$Na_2 Mo_8 O_{25}$, sodium octomolybdate.

The method of formation of these polymolybdates is similar to that of the polysilicates.

Acid solutions of molybdic acid are readily reduced by means of metallic zinc or tin. During such a reduction the color of the solution at first becomes blue, then green, and finally black, at which stage of the reaction the monoxide, Mo O, is precipitated.

When nitric acid is added to a solution of ammonium molybdate, ammonium tetramolybdate, $(N H_4)_2 . Mo_4 O_{13}$, is produced. The latter substance is of great importance in analytical chemistry, for the reason that, upon addition of phosphoric acid or a soluble phosphate, the phosphoric acid is completely separated as a constituent of a yellow precipitate known as ammonium phospho-molybdate. The latter substance has the composition expressed by the formula $(N H_4)_3 P O_4$, 11 $Mo O_3$.† When this salt is treated with *aqua regia* the the free phospho-molybdic acid, $H_3 P O_4$, 11 $Mo O_3$, goes into solution. The power which molybdic acid possesses of uniting with other acids to form complicated compounds is most important in the case of phosphoric acid; however, it is not confined to that substance alone, for similar unions of molybdic acid with arsenic and silicic acids are also known.

Molybdenum forms three sulphides, a disulphide, $Mo S_2$, a trisulphide, $Mo S_3$, and a tetrasulphide, $Mo S_4$. If, in the latter compound, we regard sulphur as having a valence of two, then molybdenum may possibly be *octovalent*. In speculating as regards the valence of molybdenum in such a compound, we must always bear in mind, however, that, as it cannot be vaporized, its molecular weight is unknown.

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* Corresponding to the *disulphate* and *dichromate*.

† More complicated formulæ have recently been assigned to ammonium phosphomolybdate and the phosphomolybdic acid. They are $(N H_4)_3 P O_4, 12 Mo O_3 + (N H_4)_2 H P O_4, 12 Mo O_3 + 8 H_2 O$ and $H_3 P O_4 . 12 Mo O_3 + 29 H_2 O$.

The tetrasulphide of molybdenum can act as an acidic anhydride, for it forms a potassium salt of the formula $K_2 Mo S_5$.

Tungsten only produces two oxides, a dioxide, $W O_2$, and a trioxide, $W O_3$,* the latter being the anhydride of tungstic acid; the element, however, is able to enter into four chlorides, namely:

Tungsten dichloride, $W Cl_2$.
Tungsten tetrachloride, $W Cl_4$.
Tungsten pentachloride, $W Cl_5$.
Tungsten hexachloride, $W Cl_6$.

The latter compound is produced by heating tungsten in a current of chlorine; it boils at 346° and has a vapor density which corresponds to the molecular weight expressed by the formula $W Cl_6$; so that tungsten must be hexavalent in the hexachloride.

Provided we regard the atoms of oxygen as always being divalent, then the highest valence of the elements of the sulphur group, when in combination with oxygen, is six and in one instance, at least, as is shown by the existence of $W Cl_6$, the valence toward chlorine also reaches that number. It seems not improbable, therefore, that, were the proper conditions attainable, the remaining elements of this family would also be able to produce compounds which, in each molecule, would contain six atoms of chlorine. We would then have a series of chlorides derived from members of the first six families which would exactly correspond to the oxides, two chlorine atoms taking the place of one of oxygen. This will be made clear from the following general formulæ:

Family	1.	2.	3.	4.	5.	6.
Chlorides Oxides	$R Cl$ $R_2 O$	$R Cl_2$ $R O$	$R Cl_3$ $R_2 O_3$	$R Cl_4$ $R O_2$	$R Cl_5$ $R_2 O_5$	$R Cl_6$ $R O_3$

The oxides of the seventh family, $R_2 O_7$, have as yet no corresponding halide, but it seems not impossible that some of the

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* An oxide, $W_3 O_8$, corresponding to $Mo_3 O_8$, is known. This oxide is probably a combination of $W O_2$ acting as a base and $W O_3$ acting as an anhydride:

$$W O_2 + 2 W O_3 = W_3 O_8.$$

missing compounds will ultimately be discovered. In the first six families, however, the highest valence of the elements toward oxygen and toward chlorine *is given by the number of the family to which each group of elements respectively belongs.*

Two tungstic acids, which correspond to $H_2 S O_4$ and $H_4 S O_5$, are known; they are $H_2 W O_4$ and $H_4 W O_5$. The first of these is a yellow powder which is produced by decomposing the aqueous solution of an alkaline tungstate with an excess of hot acid:

$$Na_2 W O_4 + 2 H N O_3 + H_2 O = 2 Na N O_3 + H_2 W O_4.$$

The second is produced by using cold instead of hot acid. A number of polytungstates which are similar to the polymolybdates are also known. Tungstic acid has the same ability of uniting with other acids to form complicated compounds as is possessed by molybdic acid. We are acquainted, for instance, with phosphotungstic acid, arsenotungstic acid, silicotungstic acid, etc. Of these compounds, perhaps the most important is *silicotungstic acid*, the sodium salt of which is formed by boiling a polytungstate of sodium* with precipitated silicic acid, the latter dissolving to form sodium silicotungstate, having a formula $Na_8 Si W_{12} O_{42} + 29 H_2 O$. This salt is extremely soluble in water and its solution has a remarkably high specific gravity.†

Uranium has the highest atomic weight and hence the most metallic nature of any of the elements under discussion. As a consequence, its trioxide can act both as a base and as an acid.

The oxides of uranium correspond exactly to those of tungsten. They are $U O_2$, *uranous oxide*, $U O_3$, *uranic oxide*, and $U_3 O_8$, which is considered to be *uranous-uranic oxide.* Only three chlorides of uranium, namely, a trichloride, $U Cl_3$, a tetrachloride, $U Cl_4$, and a pentachloride, $U Cl_5$, are known.

Uranous oxide, $U O_2$, is basic in its properties and forms salts of the general formula $U X_4$, where X represents the remainder of a monobasic acid after the removal of hydrogen. The uranous salts are colored green and are easily oxidized to compounds derived from uranic oxide.

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*Sodium paratungstate, $Na_2 W_{12} O_{41}$. This salt is formed by fusing together reinite ($Fe W O_4$) and sodium carbonate. It finds eqtensive application in the manufacture of a fireproof sizing for inflammable materials.

† The specific gravity is 3.0 when the solution is saturated at ordinary temperatures.

When *uranic oxide* enters into combination with acids it forms basic salts in which the divalent radical $U O_2$ plays the part of a divalent metal. This radical is called *uranyl* and its relationship to its salts is similar to that of the univalent radical stibionyl, Sb O—, which was described on page 243. The resemblance between the radicle uranyl and the atoms of divalent metals can be seen by comparing the following formulæ of uranyl and calcium salts:

$(U O_2) (N O_3)_2$, uranyl nitrate.	$Ca (N O_3)_2$, calcium nitrate.
$(U O_2) S O_4$, uranyl sulphate.	$Ca S O_4$, calcium sulphate.
$(U O_2)_3 (P O_4)_2$, uranyl phosphate.	$Ca_3 (P O_4)_2$, calcium phosphate.

The hydroxide from which the uranyl salts are derived can be compared to calcium hydroxide, the divalent group $U O_2$ taking the place of one atom of calcium:

$$U O_2 (O H)_2 \quad \text{and} \quad Ca (O H)_2$$

Uranylhydroxide and calcium hydroxide.

Uranyl hydroxide would, therefore, dissolve in nitric acid, for example, and would then form *uranyl nitrate*, exactly as *calcium hydroxide* would dissolve in the same reagent to form *calcium nitrate*; the two reactions can consequently be expressed as follows:

$$U O_2 (O H)_2 + 2 H N O_3 = U O_2 (N O_3)_2 + 2 H_2 O.$$
$$Ca (O H)_2 + 2 H N O_3 = Ca (N O_3)_2 + 2 H_2 O.$$

The uranyl salts are yellow with a green fluorescence.

Uranyl hydroxide, in addition to being a base is, however, also an acid; it dissolves in strong bases to form *uranates*, and by writing the formula in a manner slightly different from that given above it will be seen that uranyl hydroxide can also be called uranic acid, and therefore it corresponds to sulphuric acid:

$H_2 S O_4$, sulphuric acid, and $H_2 U O_4$, uranic acid.

The uranates, however, in formula resemble the disulphates and dichromates, and not the sulphates and chromates. When a uranyl salt is treated with a solution of a caustic alkali, the first change would be the formation of uranyl hydroxide (uranic acid):

$$U O_2 (N O_3)_2 + 2 K O H = U O_2 (O H)_2 + 2 K N O_3;$$

this, however, reacts with the excess of alkali to form a diuranate:

$$2 U O_2 (O H)_2 + 2 K O H = K_2 U_2 O_7 + 3 H_2 O.$$

Sodium uranate, $Na_2U_2O_7$, is a yellow powder which, under the name of uranium yellow, is used in coloring glass, to which it imparts a yellow tint with a green fluorescence.

The chief compounds discussed in the last chapter are given in the following tables:

CHLORIDES.				OXIDES.			
$Cr Cl_2$	$Mo Cl_2$	$W Cl_2$	—	$Cr O$*	$Mo O$	—	—
$Cr Cl_3$	$Mo Cl_3$	—	—	$Cr_2 O_3$‡	$Mo_2 O_3$*	—	—
	$Mo Cl_4$	$W Cl_4$	$U Cl_4$	—	$Mo O_2$§	$W O_2$	$U O_2$*
	$Mo Cl_5$	$W Cl_5$	$U Cl_5$	$Cr O_3$†	$Mo O_3$†	$W O_3$†	$U O_3$‡
		$W Cl_6$	—				
				$Cr_3 O_4$	$Mo_3 O_8$	$W_3 O_8$	$U_3 O_8$

* Basic.

† Acidic.

‡ Basic and acidic.

§ The solution of $Mo O_2$ reddens litmus paper, but possesses no other acid properties.

The oxides on the last line are considered to be combinations of two other oxides.

ACIDS.				DI AND POLY ACIDS.
$Cr O_3$	$Mo O_3$	$W O_3$	$U O_3$	All of these elements also form salts derived from a di-acid having the general formula $H_2 X_2 O_7$, and they also form salts derived from complicated poly-acids; the latter are formed by uniting 3, 4, 5, etc., formula weights of the acids $H_2 X O_4$ and then separating water until a dibasic acid is left.
—	$H_2 Mo O_4$	$H_2 W O_4$	$H_2 U O_4$†	
—	$H_4 Mo O_5$	$H_4 W O_5$	$H_4 U O_5$*	
—	$H_6 Mo O_6$*	—		

* Existence doubtful.

† Also acts as a basic hydroxide, uranyl hydroxide, $U O_2 (O H)_2$.

The above acids are all *dibasic* (see page 149).

CHAPTER LVIII.

THE ELEMENT FORMING THE PRIMARY GROUP OF THE SEVENTH FAMILY.

Manganese, symbol Mn, atomic weight 55.

Only one element which should undoubtedly have its place in the primary group of the seventh family has as yet been discovered, and that element is manganese. Manganese, having its place at the middle of one of the long periods, must necessarily differ quite markedly from the typical elements of the family, namely, the halogenes; and, indeed, a great variation in properties is to be expected, even without any such consideration, for manganese is metallic in its nature, while fluorine, chlorine, bromine and iodine are the most negative of all the elements. As a consequence, we would expect the greatest resemblance between the latter group and manganese to lie in the derivatives of the highest oxide of that element, in which compounds the metallic nature of manganese is almost entirely overshadowed by the negative elements with which it is combined, and, indeed, we observe that the permangates, $R\ Mn\ O_4$,* in many respects, such as isomorphism, solubility, etc., are very much like the perchlorates. The lower oxides of manganese, on the other hand, bear no resemblance to the halogene oxides, in fact, their nearest prototypes are to be found among the oxides of iron, chromium, cobalt, nickel or lead, while in many respects $Mn\ O$ acts very much like the oxides of calcium, magnesium or zinc. The typical oxide of the seventh family, therefore, would be $X_2\ O_7$; in no case, excepting that of manganese, has it been isolated; it is, however, known in its derivatives (permanganates, perchlorates, periodates and the corresponding acids).

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*R represents a univalent metal.

Manganese is never found as the uncombined element. The chief minerals in which it occurs are given in the following table:

Braunite, $Mn_2 O_3$.
Hausmannite, $Mn_3 O_4$.
Pyrolusite (polianite), $Mn O_2$.
Manganite, $Mn O (O H)$.*

Pyrolusite and manganite are the most important ores of manganese. They both occur in large beds and veins. Manganous oxide, $Mn O$, is also sometimes found as a mineral called manganosite. The carbonate, rhodochrosite, $Mn C O_3$, belongs to the calcite group (see page 393), while manganocalcite, $(Mn, Ca) C O_3$, probably is isomorphous with arragonite.

The element itself is very difficult to separate from its ores, for such powerful reducing agents as red hot charcoal or hydrogen are only able to change the higher oxides into manganous oxide, but not into manganese.† Manganese can, however, be isolated either by heating manganous chloride with sodium, or by electrolysis of the fused chloride or fluoride.

Manganese is a greyish white metal somewhat resembling cast iron; it is crystalline in structure and brittle, although it possesses a certain amount of toughness. The specific gravity is about 8 and its atomic volume 6.9. Manganese is, therefore, at the minimum of one of the curves of atomic volumes§; the element with next smaller atomic weight has a larger atomic volume, and, as a consequence, manganese is difficult to fuse and forms *colored salts.* The melting point of manganese lies at about 1900°; this is somewhat higher than that of iron. Pure manganese, after polishing, rapidly becomes dull when exposed to the air, owing to oxidation. The metal is energetically attacked by acids.‡ Pure manganese has no technical application; an alloy of manganese and iron (ferro-manganese, *spiegeleisen*) is, however, of the greatest commercial importance for the manufacture of Bessemer steel.

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* Corresponding to $Al O (O H)$. Trivalent manganese can replace aluminium and chromium isomorphously in the spinells.

† The conversion of the oxides into metallic manganese by means of charcoal takes place only at a high white heat.

‡ Impure manganese even decomposes water very readily.

§ A diagram, plotted with the atomic volumes as ordinates and atomic weights as abscissae is appended after the index.

Manganese forms the following oxides:

$Mn\,O$, manganous oxide.
$Mn_2\,O_3$, manganic oxide.
$Mn_3\,O_4$, manganous-manganic oxide.
$Mn\,O_2$, manganese dioxide (manganese hyperoxide, black oxide of manganese).
$Mn_2\,O_7$, permanganic anhydride.

Manganous oxide is basic in its character; it readily dissolves in acids to form the *manganous* salts; this oxide can be produced through reduction of any one of the higher oxides by means of heating the same in a current of hydrogen. It is green, or greyish green, in color, and, when exposed to the air, it readily absorbs oxygen to form $Mn_3\,O_4$.* *Manganous hydroxide,* $Mn\,(O\,H)_2$, is separated as a white precipitate when alkaline solutions or ammonia water are added to a solution containing a manganous salt; precipitation by means of ammonia is, however, entirely prevented by by the presence of ammonium salts, for manganous salts have a tendency to form double salts with the compounds of ammonium, identical with that displayed by the similar compounds of zinc or magnesium (see pages 396 and 402). When exposed to the air, manganous hydroxide rapidly turns brown, because it absorbs oxygen and is converted into manganous-manganic oxide, $Mn_3\,O_4$; when dissolved in acids, the corresponding manganous salts are produced. The latter do not spontaneously oxidize when exposed to the air.

Manganous chloride is contained in the colorless solutions obtained by dissolving any one of the oxides of manganese in hydrochloric acid.† When slowly evaporated the solutions deposit pinkish colored tablets of the formula $Mn\,Cl_2 + 4\,H_2\,O$. The anhydrous salt cannot be obtained from these by heating, because the chloride, at a temperature high enough to drive off water of crystallization, loses chlorine, absorbs oxygen and in part changes into $Mn_3\,O_4$. In order to obtain the chloride in an anhydrous condition, the water of crystallization must be driven off in a current of dry hydrochloric acid gas. Manganous chloride is extremely soluble in water and shows the greatest tendency to form double chlorides with the corresponding salts of other metals.

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*This action may become so violent as to cause the whole mass to glow.

† Should an oxide containing more oxygen than Mn O be dissolved, the excess of oxygen will oxidize the hydrochloric acid, liberating chlorine (see page 58).

Manganous sulphate is produced by dissolving any one of the oxides of manganese in hot sulphuric acid,* or better, by dissolving the carbonate in the same acid, diluted. Upon evaporating and cooling to below 6°, crystals having the formula $Mn\,S\,O_4 + 7\,H_2O$ separate. The latter are isomorphous with the vitriols (see page 394). If the temperature of crystallization is between 7° and 20°, then the crystals contain but five molecules of water and are isomorphous with ordinary sulphate of copper (blue vitriol; see page 381). The sulphate is readily soluble in water.

Manganous carbonate is insoluble in water and is therefore preciptiated from solutions of manganous salts by the addition of a soluble carbonate. The naturally occurring salt is isomorphous with calcite.

Manganous sulphide is insoluble in water but soluble in dilute acids† (see page 95); it is therefore precipitated from solutions containing manganous salts by the addition of an alkaline sulphide solution:

$$Mn\,S\,O_4 + (N\,H_4)_2\,S = (N\,H_4)_2\,S\,O_4 + Mn\,S.$$

Manganous sulphide is a flesh-colored precipitate which readily absorbs oxygen from the air, while, at the same time, it turns of a brown color.

Manganic oxide, $Mn_2\,O_3$, occurs in nature as the mineral braunite, which is the hardest ore of manganese. In the laboratory it can be produced by heating manganous oxide, manganese dioxide or manganous-manganic oxide to red heat in a currrent of hydrogen. The oxide is black in color, insoluble in water and, when heated to a white heat, changes to $Mn_3\,O_4$. The hydroxide $Mn\,O_2\,H$, corresponding to $Al\,O_2\,H$, occurs as the mineral manganite; this compound can also be formed by slow oxidation of manganous hydroxide, $Mn\,(O\,H)_2$, in the air, but, if the manganous hydroxide is covered with ammonia solution, then the product of oxidation is the normal manganic hydroxide, $Mn\,(O\,H)_3$. Both the oxide and hydroxides are weakly basic in character. The salts derived from them are unstable and resemble those derived from the oxide of aluminium, $Al_2\,O_3$. They are decomposed by the addition of an excess of water. Their solutions are dark brown in color and on addition of alkalis precipitate manganic hydroxide.

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* When an oxide of manganese containing more oxygen than Mn O is dissolved, then the excess of oxygen passes off as such.

† Even in acetic acid (difference from zinc sulphide).

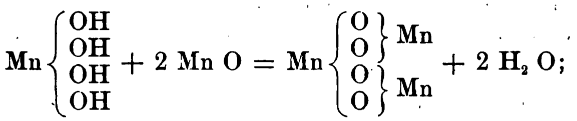
Manganic chloride, $Mn\,Cl_3$, is produced by dissolving manganic hydroxide in cold hydrochloric acid. The solution has a dark brown color and, on standing, liberates chlorine, leaving *manganous chloride* behind.

Manganic sulphate, $Mn_2\,(S\,O_4)_3$, is a deep green, amorphous powder which is produced by heating finely divided manganese dioxide with concentrated sulphuric acid to 110°. A portion of the oxygen of the dioxide then passes off, while manganese sulphate remains. The reaction can be considered as taking place in two stages:

1. $2\,Mn\,O_2 = Mn_2\,O_3 + O$
2. $Mn_2\,O_3 + 3\,H_2\,S\,O_4 = Mn_2\,(S\,O_4)_3 + 3\,H_2\,O.$

If the heating be carried too far, more oxygen will be evolved and manganous sulphate, $Mn\,S\,O_4$, will remain. Manganic sulphate is interesting because it forms compounds with the sulphates of the alkali metals which are isomorphous with the alums, this fact illustrating the close resemblance between trivalent manganese, aluminium, chromium and iron. Potassium-manganic sulphate has the formula $K_2\,S\,O_4,\ Mn_2\,(S\,O_4)_3 + 24\,H_2\,O$ (see page 327).

Manganous-manganic oxide, $Mn_3\,O_4$, occurs as a brownish-black, crystalline mineral known as hausmannite, it is produced by heating any of the other oxides of manganese, when in contact with the air, to a red heat.[*] Manganous-manganic oxide is considered as being a *manganous* salt of *ortho* manganous acid (the hydroxide of manganese dioxide, $Mn\,(O\,H)_4$, being designated as *manganous acid*).[†] This theory is expressed by the following formula:



$$Mn\begin{cases}OH\\OH\\OH\\OH\end{cases} + 2\,Mn\,O = Mn\begin{cases}\left.\begin{matrix}O\\O\end{matrix}\right\}Mn\\\left.\begin{matrix}O\\O\end{matrix}\right\}Mn\end{cases} + 2\,H_2\,O;$$

$$Mn\,(O\,H)_4 + 2\,Mn\,O = Mn_3\,O_4 + 2\,H_2\,O;$$

and is borne out by the fact that manganous-manganic oxide, when treated with dilute nitric or sulphuric acid, forms *manganous* nitrate or sulphate, while *manganese dioxide* is left behind:

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[*] The oxide $Mn_2\,O_3$ is stable when in an atmosphere of oxygen, if the temperature is no higher than that of a Bunsen burner. At white heat it is also converted into $Mn_3\,O_4$.

[†] Manganous acid would thus be parallel with sulphurous acid:—$S\,O_2$, sulphur dioxide; $H_2\,S\,O_3$, sulphurous acid; $H_4\,S\,O_4$, orthosulphurous acid. $Mn\,O_2$, manganese dioxide; $H_2\,Mn\,O_3$, manganous acid; $H_4\,Mn\,O_4$, orthomanganous acid.

1. $Mn\ O_4\ Mn_2 + 4\ H\ N\ O_3 = Mn\ (O\ H)_4 + 2\ Mn\ (N\ O_3)_2$.
2. $Mn\ (O\ H)_4 = Mn\ O_2 + 2\ H_2\ O$.

This reaction is similar to that encountered with $Pb_3\ O_4$ (see page 312).

Manganese dioxide, $Mn\ O_2$, is probably the most important compound of manganese. It occurs in large quantities as a mineral which is named pyrolusite. The latter has a steel-grey color, metallic lustre and crystallizes in prisms belonging to the rhombic system. A considerable amount of this oxide is mined in the New England States and in California. Manganese dioxide can be prepared artificially by oxidizing manganous carbonate with an alkaline solution of chlorine (see pages 115 and 116).

Manganese dioxide, when heated to a high red heat, loses one-third of its oxygen and changes into manganous-manganic oxide (see page 18):

$$3\ Mn\ O_2 = Mn_3\ O_4 + 2\ O.$$

During this decomposition the dioxide first changes into manganic oxide, $Mn_2\ O_3$, and then the latter compound loses the quantity of oxygen necessary to produce $Mn_3\ O_4$ as the temperature is increased to a high red heat. Acids decompose manganese dioxide. When acting in the cold they not infrequently produce *manganic* salts, while the surplus of oxygen is liberated (see page 437); on the other hand, hot acids leave *manganous* salts behind. Of course, if any oxidizable substance is present, the liberated oxygen does not pass off as such, but is used up in the work of oxidation. The reaction when warm sulphuric acid is brought in contact with manganese dioxide is as follows:

$$Mn\ O_2 + H_2\ S\ O_4 = Mn\ S\ O_4 + H_2\ O + O,$$

but, on the other hand, hydrochloric acid, because it is readily oxidized, liberates *chlorine:*

$$Mn\ O_2 + 4\ H\ Cl = Mn\ Cl_2 + 2\ H_2\ O + 2\ Cl.$$

In the latter case it is not at all improbable that $Mn\ Cl_4$ is at first formed and that the latter salt subsequently breaks down into manganous chloride and chlorine (see pages 58 and 59).* The reactions of manganese dioxide are very similar to those of the corresponding compound of lead (see page 312). Several hydroxides related to manganese dioxide are known. The simplest of these is $Mn\,O\,(O\,H)_2$. The hydroxides have *acidic properties** and form salts which are designated as *manganites*. However, none of the latter are derived from the simple ortho or meta-hydroxides — $Mn\,(O\,H)_4$ or $Mn\,O\,(O\,H)_2$ — but, like the salts of so many acids which we have already studied, they are produced by complicated poly-manganous acids. Two examples of the latter are $H_2\,Mn_2\,O_5$ and $H_2\,Mn_5\,O_{11}$; their formation might be imagined as taking place as follows:

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* Recent investigations render it probable that the chloride $Mn\ Cl_4$, when formed, assumes the part of an acidic anhydride and, uniting with the excess of hydrochloric acid, which is present, forms an acid of the formula $H_2\ Mn\ Cl_6$, analogous to $H_2\ Si\ F_6$

1. $2\,Mn\,O\,(O\,H)_2 = H_2\,Mn_2\,O_5 + H_2\,O.$
2. $5\,Mn\,O\,(O\,H)_2 = H_2\,Mn_5\,O_{11} + 4\,H_2\,O.$

Potassium pentamanganite, $K_2\,Mn_5\,O_{11}$, is formed by passing carbon dioxide into a solution of potassium manganate.

Calcium dimanganite, $Ca\,Mn_2\,O_5$, is important because, when treated with hydrochloric acid, it generates chlorine:

$Ca\,O,\,2\,Mn\,O_2 + 10\,H\,Cl = Ca\,Cl_2 + 2\,Mn\,Cl_2 + 5\,H_2\,O + 4\,Cl.$

This salt is readily produced by heating a mixture of manganous hydroxide and calcium hydroxide in a current of air, so that a method† of utilizing the waste manganous chloride, which was formerly lost during the commercial preparation of chlorine, has been founded on this reaction.

When manganese dioxide is fused with a caustic alkali in the presence of an oxidizing agent, or even in the air, a *manganate* is produced. The *manganates*, in chemical composition, are analogous to the sulphates, chromates and molybdates, etc. This will be seen from the following formulæ:

$K_2\,Mn\,O_4$, potassium manganate.
$K_2\,Cr\,O_4$, potassium chromate.
$K_2\,Mo\,O_4$, potassium molybdate.

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and to other similar compounds which we have encountered (see pages 291, 305, 318). The compound $H_2\,Mn\,Cl_6$ then breaks down as follows:

$$H_2\,Mn\,Cl_6 = 2\,H\,Cl + Mn\,Cl_2 + 2\,Cl.$$

It is, however, very certain that the compound is not alone present in the beginning of the reaction between hydrochloric acid and manganese dioxide, for manganese trichloride, $Mn\,Cl_3$, is also produced:

$$Mn\,O_2 + 4\,H\,Cl = Mn\,Cl_3 + Cl + 2\,H_2\,O.$$

The whole matter may therefore be regarded as not as yet definitely settled.

*The hydroxide of manganese dioxide, $Mn\,O\,(O\,H)_2$, is sufficiently acid in its properties to redden blue litmus paper and to expel carbonic acid from the carbonates of the alkalis. Several of the hydroxides are found as minerals; they are termed "wad."

† Weldon's process.

However, those manganates which are soluble in water, differ very markedly from their prototypes in one particular; they are very readily decomposed by the addition of an excess of the solvent and are only stable in alkaline solution. In so decomposing, they change into *permanganates* and manganese dioxide. The manganates, when dry, have a deep red color. They are powerful oxidizers and only the salts of the alkali metals are soluble in water. The solutions are green, but change to red on addition of an acid.* Neither manganic acid, $H_2 Mn O_4$, nor its anhydride, $Mn O_3$, have been isolated.

The anhydride of permanganic acid, $Mn_2 O_7$, is the only one of the oxides, lying in genetic relationship to the acids of the chlorine family which represent the highest stage of oxidation, which has been isolated. It is a dark green, almost black, oily liquid produced by adding potassium permanganate, in small quantities, to concentrated sulphuric acid. The liquid must be cooled by means of a mixture of snow and salt during the process, and, after the operation is completed, warmed to 60°, when the anhydride distils. $Mn_2 O_7$ is extremely unstable; if allowed to stand it spontaneously liberates oxygen and leaves manganic oxide, $Mn_2 O_3$; it is a most powerful oxidizer; paper or alcohol are instantly ignited by it. When added to water it forms permanganic acid:

$$Mn_2 O_7 + H_2 O = 2 H Mn O_4.$$

Permanganic acid is entirely analogous to perchloric acid. It can be produced by decomposing a solution of barium permanganate with exactly the requisite amount of sulphuric acid. By means of the ensuing double decomposition, insoluble barium sulphate and permanganic acid are produced:

$$Ba (Mn O_4)_2 + H_2 S O_4 = Ba S O_4 + 2 H Mn O_4;$$

the red solution so formed is then evaporated to dryness, when permanganic acid remains in the form of a reddish-brown, crystalline substance. Permanganic acid is quite unstable, it breaks down,

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* Due to the formation of a permanganate:

$$5 K_2 Mn O_4 + 4 H_2 S O_4 = 4 K Mn O_4 + Mn S O_4 + 3 K_2 S O_4 + 4 H_2 O.$$

When water, and not acid, is added to the manganate, a hydroxide derived from $Mn O_2$ is formed:

$$3 K_2 Mn O_4 + 3 H_2 O = 2 K Mn O_4 + Mn O (O H)_2 + 4 K O H.$$

The potassium hydroxide will then react with the hydroxide of manganese to form a manganite. Very weak acids (such as carbonic acid) facilitate the change.

when exposed to the light, and its solutions, like those of perchloric acid, are powerful oxidizers.

The most important permanganate is the *permanganate of potassium;* this salt is produced, as was mentioned on page 440, by fusing manganese dioxide with a mixture of potassium hydroxide and an oxidizing salt (such as potassium nitrate or potassium chlorate*); the dark green flux then contains *potassium manganate,* the latter is converted into the permanganate by dissolving in water and then passing carbon dioxide into the solution.† Potassium permanganate crystallizes in long prisms, belonging to the monoclinic system, the crystals are dark green, almost black in color, their solution in water has an intense reddish-purple color; the salt is a most powerful oxidizing agent. In oxidizing with potassium permanganate there is an essential difference between the action of the salt in *acid* or in *alkaline* solution; in the former event the permanganate changes to a *manganous* salt, in the latter to manganese dioxide, respectively to a manganite.

1. *Acid solution.*

$$2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,O + 3\,H_2O.$$

Alkaline solution.

a. $2\,KMnO_4 + 2\,KOH = 2\,K_2MnO_4 + H_2O + O;$

b. $2\,K_2MnO_4 + 2\,H_2O = 4\,KOH + 2\,MnO_2 + 2\,O.$

The first change, in alkaline solution, is, therefore, from the permanganate to the manganate, the second from the manganate to manganese dioxide; of course, the latter substance subsequently produces a *manganite* with the excess of caustic potash which is present; from these equations it follows that, for every two formula-weights of potassium permanganate in acid solution, there are five atoms of oxygen to be used in oxidation, while for every two formula weights in alkaline solution, there are but

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* The oxygen of the atmosphere is also able to effect the change.

† The reaction is as follows:

$$3\,K_2MnO_4 + 2\,CO_2 = 2\,K_2CO_3 + 2\,KMnO_4 + MnO_2;$$

the reactions taking place on the addition of water or of sulphuric acid are given on page 440, foot note.

three; the following two equations illustrate the application of these rules:

$$2\,K\,Mn\,O_4 + 3\,H_2\,S\,O_4 + 5\,H_2\,S\,O_3 = K_2\,S\,O_4 + 2\,Mn\,S\,O_4 + 5\,H_2\,S\,O_4 + 3\,H_2\,O.$$

$$2\,K\,Mn\,O_4 + 3\,Na_2\,S\,O_3 + H_2\,O = 2\,K\,O\,H + 2\,Mn\,O_2 + 3\,Na_2\,S\,O_4.$$

Owing to its oxidizing powers, potassium permanganate is frequently used as a disinfecting agent.

Manganese, with its diversity of compounds, in which it displays such a great difference in valence, serves admirably to illustrate the fact that the chemical behavior of an element is, to a large extent, relative, and that the properties of its compounds depend just as much *upon the elements with which it is united, and upon the manner of such union, as it does upon the individual characteristics of the element itself.* Manganese, when entering into the formation of manganous salts, is far more like magnesium or zinc than it is like manganese in the manganates or permanganates; when manganic oxide, as a base, has united with acids to form manganic salts, then manganese resembles trivalent chromium, iron or aluminium even to such an extent that its sulphate will form alums; in the manganates the element may be compared to sulphur in the sulphates while, lastly, the permanganates are analogous to the perchlorates or periodates. One essential distinction, however, remains as existing between the various compounds of manganese and the elements with which it has been compared; the compounds of manganese can be converted the one into the other, while, of course, those of zinc, for example, can never be changed into those of chromium or those of iron into those of chlorine; *oxidizing* agencies transform *manganous* salts into *manganic* salts, *manganese dioxide, manganates* and *permanganates successively*, while, on the other hand, reducing agencies, beginning with the permanganates, produce exactly the opposite result.

The relationship between the compounds of manganese and those of a few other elements can be seen from the following table:

Manganous compounds (Oxide, $Mn\,O$)	Sulphate, $Mn\,S\,O_4 + 7\,H_2\,O$ Nitrate $Mn\,(N\,O_3)_2$ Chloride, $Mn\,Cl_2$	like	$Zn\,S\,O_4 + 7\,H_2\,O$ $Mg\,(N\,O_3)_2$ $Ca\,Cl_2$
Manganic compounds (Oxide, $Mn_2\,O_3$)	Sulphate, $Mn_2\,(S\,O_4)_3$ Alum, $Mn_2\,(S\,O_4)_3\,K_2\,S\,O_4,\,24\,H_2\,O$	like	$Al_2\,(S\,O_4)_3$ $Al_2\,(S\,O_4)_3\,K_2\,S\,O_4,\,24\,H_2\,O$

Manganates (Acid, $H_2 Mn O_4$)	Potassium manganate. $K_2 Mn O_4$ Barium manganate, $Ba Mn O_4$	like	$K_2 S O_4$ or $K_2 Cr O_4$ $Ba S O_4$ or $Ba Cr O_4$
Permanganates (Acid, $H Mn O_4$)	Potassium permanganate, $K Mn O_4$ Barium permanganate, $Ba (Mn O_4)_2$	like	$K Cl O_4$ $Ba (Cl O_4)_2$

The oxides of manganese are, perhaps, most like those of lead, but, in formula, they also resemble those of the type of the family, chlorine.

OXIDES OF CHLORINE.	LEAD.	MANGANESE.
$Cl_2 O$	———	———
$Cl O$	$Pb O$	$Mn O$
$Cl_2 O_3$	$Pb_2 O_3$	$Mn_2 O_3$
$Cl O_2$	$Pb O_2$	$Mn O_2$
$(Cl_2 O_7)$	———	$Mn_2 O_7$
	$Pb_3 O_4$	$Mn_3 O_4$

This process of comparison, were space to permit, could be carried much farther, and, indeed, the formation of tables like the above would be a most instructive exercise for the pupil.

CHAPTER LIX.

IRON, COBALT AND NICKEL.

Iron, symbol Fe, atomic weight 56.
Cobalt, symbol Co, atomic weight 59.
Nickel, symbol Ni, atomic weight 58.7.

Iron, cobalt and nickel are members of the eighth family of elements, which consists of three groups, each of which contains three individuals, namely:

1. Iron, cobalt, nickel.
2. Rhuthenium, rhodium, palladium.
3. Osmium, iridium, platinum.

The properties of these elements are such that they form a gradual transition from the last elements of the first halves of the long periods to the first ones in the second; so that we would expect iron to be very much like manganese and nickel to bear marked resemblance to copper, and, indeed, such is the case. The valence of the elements in their highest oxides, passing from manganese, through iron, cobalt and nickel, to copper, diminishes with each successive individual, as the atomic weight increases; manganese, in the permanganates, has a valence of seven, iron, in ferric acid, a valence of six, cobalt a valence of three in the oxide $Co_2 O_3$, nickel, almost without exception, forms compounds derived from $Ni O$, while, lastly, copper can appear as a univalent metal in its *cuprous* form.

	Mn.	Fe.	Co.	Ni.	Cu.
Highest valence,	VII	VI	III	II*	I (II)
Oxides,	$Mn_2 O_7$	$Fe_2 O_6$	$Co_2 O_3$	$Ni_2 O_2$	$Cu_2 O$.

Iron, cobalt and nickel are near the minimum of the curve of atomic volumes formed in the period of which they are members, while the elements which follow in the same period show a rapid increase in their atomic volumes as we pass along the series in the direction of increasing atomic weights, the three individuals in question are therefore malleable and ductile, have high melting points[*] and form colored salts. The physical constants mentioned in this connection are given on the following table:

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* Nickel *can* form an oxide $Ni_2 O_3$, but the latter forms no salts, and is decomposed with the greatest of ease.

	Atomic weight.	Specific gravity.	Atomic volume.	Melting point.
Iron.	56.	7.8	7.2	1770° (?)
Cobalt,	59.	8.5	6.9	1750°
Nickel.	58.7	8.8	6.7	1570°

Nickel, owing to its chemical reactions, specific gravity, atomic volume and melting point apparently has its position in the periodic system immediately following that of cobalt, although its atomic weight is somewhat less than that of the latter element; it seems probable, therefore, that, at some future time, more exact study will prove the atomic weights of the two elements in question to have been inaccurately determined[†]; if this should not prove to be the case, however, then cobalt and nickel certainly form a most remarkable exception to Mendelejeff's rule in the arrangement of that system.

The principal minerals in which iron, cobalt and nickel occur are as follows:

Native iron.—The occurrence of masses of iron of terrestial origin has been mentioned several times, but is not beyond doubt. Meteoric iron is not infrequently found, it usually contains from 1 to 20 per cent. of nickel, these meteorites contain the metal arranged in striæ with a differing contents of nickel, so that, as they offer a differing resistance to acids, meteoric iron, when polished and subjected to the corroding action of reagents, will show a surface marked by regular etchings.

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[*] The melting points are, however, lower than those of the elements immediately preceeding which have *diminishing* atomic volumes with *increasing* atomic weights.

[†] Gerhardt Krüss has recently published some work in which he undertakes to show that what has hitherto been regarded as pure nickel in reality contains an admixture of one, or more, hitherto undiscovered elements and that the same is probably true of cobalt. Some of the fractions into which Krüss divided nickel have an atomic weight lying between 56 and 58, the others between 60 and 100; of course in view of these results, the atomic weights of cobalt and nickel are as yet undetermined. Clemens Winckler, however, in view of his previous investigations of the atomic weight of nickel and in view of a review of some parts of his former work, which he instituted with apparently pure materials, doubts Krüss's results, so that, until further light is thrown on the subject, the old theories as regards cobalt and nickel must be maintained. See Krüss and Schmidt, Berichte d. Deutsch. Chem. Gesell. 22; 11 and 2026; Clemens Winckler, ibid, 890.

Iron pyrites, $Fe S_2$ occurs in rocks of all ages, it isomorphous with *arsenical pyrites*, $Fe As S$, with the sulphide of manganese, $Mn S_2$ (Hauerite) and with the sulphides and arsenides of cobalt and nickel, having the general formulæ $M S_2$, $M As_2$ or $M As S$. Iron pyrites is *dimorphous*, for a mineral of the same formula, belonging to a different crystalline system, is known, this mineral is called markasite.

Ferrous sulphide, $Fe S$, is found as troilite.

A ferric sulphide, $Fe_2 S_3$, frequently plays the part of an acidic anhydride and with bases, such as $Cu_2 S$, $Ag_2 S$ or $Cu S$, forms minerals of which *chalcopyrite*, $Cu_2 S, Fe_2 S_3 = 2 Cu Fe S_2$, is an example (see page 376).

Hematite (specular iron) is *ferric oxide*, $Fe_2 O_3$. It is one of the most important iron ores and occurs in rocks of all ages.

Magnetite (magnetic iron ore) is ferrous ferric oxide, $Fe O, Fe_2 O_3 = Fe_3 O_4$. This oxide is isomorphous with the spinells (page 326) and is probably similarly constituted.

Various hydroxides of ferric oxide are also frequently met with. The chief representative of this most important class of minerals is *limonite* (brown hematite) $Fe_4 O_9 H_6 = 2 Fe_2 O_3 + 6 H_2 O$.

Siderite (spathic iron) is ferrous carbonate. $Fe C O_3$. It occurs in many rock strata, in gneiss, mica slate, clay slate and with the coal formation. It is isomorphous with *calcite.*

Iron is also found as a constituent of a large number of silicates. In consequence of the disintegration of the rocks in which it occurs, it finds its way into the soil and into the natural waters. It is an invariable constituent of chlorophyll (the green coloring matter of leaves) and it is always found in the haemoglobin of the blood.

Cobalt chiefly occurs as *cobaltite*, $Co As S$ ($Co S_2 + Co As_2$), isomorphous with iron pyrites;* as *smaltite*, $Co (Fe Ni) As_2$, also isomorphous with iron pyrites; and as *danaite*, $(Fe, Co) (As S)_2$, isomorphous with *markasite.* Cobaltous carbonate, (sphaerocobaltite) $Co C O_3$, is also sometimes found, as well as the arsenate, $Co_3 (As O_4)_2 + 8 H_2 O$, which is called *erythrite.*

Nickel occurs in meteorites as an alloy of iron; as *gersdorfite*, $Ni As S$, isomorphous with cobaltite and iron pyrites; as the arsenide, *niccolite*, $Ni As$ (isomorphous with zinc blende, page 403); as a basic carbonate, and as the arsenate.

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* As might be expected. cobalt replaces iron isomorphously, but in this mineral we have another phenomenon which is not so self-evident, namely *arsenic* replaces *sulphur* isomorphously. This substitution is not infrequent in the group of minerals of which iron pyrites is the representative (see page 224).

Iron, cobalt and nickel are all easily reduced from their oxides by means of charcoal. *The metallurgy of iron* is among the most important commercial operations of the present time. In the preparation of this metal the most important ores are the *oxides, hydroxides* and the *carbonate*. The ores are crushed and roasted for the purpose of burning the sulphides, expelling the water and changing the oxides as much as possible into ferric oxide, $Fe_2 O_3$. They are then reduced in a blast furnace. The latter consists of a shaft, varying in height from fifty to ninety feet, with a maximum diameter of from fourteen to seventeen feet, the shaft being shaped like two truncated cones united at their bases; below these is a circular chamber or hearth which is built of stone or firebrick and which is open at one side. The remainder of the furnace is constructed of firebrick and encased in boiler iron. The *blast* is introduced through two openings, termed tuyères, at the bottom of the furnace and the air which is forced in through these is heated by means of the waste gases passing from the furnace. The furnace is charged with alternate layers of calcined iron ore, coke or charcoal, and limestone. The latter substance, uniting with the siliceous matter* which is present in the ore, forms a fusible glass called the *slag*, which surrounds the finely divided metal during the first stages of the reduction and prevents oxidation.† The slag is allowed to run off over a dam which is sufficiently high to retain the molten iron in the furnace.

The chemical changes which take place in a blast furnace are quite complicated, and all of them are not, as yet, definitely understood; however, the most important reactions in the production of cast iron are as follows. The carbon, uniting with the oxygen entering from the tuyères, forms carbon dioxide, and the latter, in passing over red hot coke or charcoal, is reduced to carbon monoxide (see page 275); hot carbon monoxide now comes in contact with the descending charges of ore and reduces the oxide to a spongy form of iron, which soon becomes coated with slag:

$$Fe_2 O_3 + 3\ CO = 2\ Fe + 3\ CO_2;$$

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*Feldspar, slate, quartz, etc.

†If the ore contains limestone in sufficient or excessive quantity, it may be necessary to add siliceous matter such as feldspar. The lime prevents the formation of a ferruginous slag, which would entail a loss of iron.

the portion of the furnace in which this reduction occurs has a temperature of from 600° to 900°. The spongy metal passes downward in the furnace, the temperature increasing to 1000° at the widest part of the furnace; at this point the iron takes up carbon to form a chemical combination with that element, and, at a lower zone, when the temperature is about 1400°, the mass, which has been in a pasty condition, melts and runs down into the hearth. The latter is tapped from time to time and the iron cast into semicylindrical molds called "pigs." Pig iron is quite impure, it contains carbon, phosphorus, silicon, sulphur and manganese and is divided into two chief classes, *white cast iron** and *grey cast iron;* the former contains its carbon chemically united with the iron, the latter, in consequence of the presence of silicon, has separated the greater portion of its carbon in the form of graphite; the proportion of carbon in white iron is from .2 to 2.67 per cent.; in grey iron, combined carbon, .04 to .618 and graphite from 1.8 to 4.4 per cent.; if the iron ore contained a considerable quantity of manganese, the latter is reduced with the iron and the alloy so formed is capable of taking up a considerably greater quantity of carbon (as high as 6.9 per cent.) this form of iron is known as *spiegeliron.* Cast iron is brittle, easily fusible, and cannot be welded or tempered, when treated with hydrochloric acid it dissolves, while the combined carbon passes off in the form of hydrocarbons which possess a most disagreeable odor,† the graphite remains undissolved.

Wrought iron is produced from cast iron either by *puddling* or *cementation;* the first method consists of melting cast iron in contact with the air and then blowing hot air through the mass of metal, by this means the carbon, phosphorus, silicon, etc., are burned out and removed; the second method consists in melting cast iron with pure ferric oxide, the latter oxidizing the impurities which are present. Wrought iron contains less than .6 per cent. of carbon‡ and very small amounts of silicon and phosphorus, it possesses a fibrous texture, is malleable and ductile and melts at about 1900°.

Steel contains more carbon than wrought iron, and generally less than cast iron; it is produced by the process of *cementation* or by the *Bessemer* steel process. Cementation steel is produced by heating wrought iron with powdered charcoal until it has taken up the requisite amount of carbon, or by fusing pure wrought iron with an impure iron containing carbon (spiegeliron), the quantity of the latter being adjusted so as to form the product required.

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* White cast iron is formed at a lower furnace temperature than grey cast iron or spiegeliron.

† The odor has also been attributed to phosphine.

‡ When it contains more than .6 per cent. it is steel.

The *Bessemer steel* process produces steel directly from cast iron; it consists, briefly, of first burning out the impurities in melted cast iron, by placing the latter in a large crucible and forcing air in through the bottom and then, after stopping the blast, of adding spiegeliron[*] until the requisite amount of carbon is present. Bessemer steel is used in the manufacture of rails and of other large steel implements; it contains from .7 to 2.4 per cent. of combined carbon. When steel is heated and rapidly cooled, by plunging into water, it becomes very hard and brittle, this hardened steel, when once more heated and allowed to cool slowly, becomes elastic, the process being called tempering; the metal is capable of taking a very high polish.

Chemically pure iron can be prepared by reducing either the pure oxide, oxalate or chloride of iron in a current of hydrogen, it has a specific gravity of 7.84 and a melting point between 1550° to 1600°,[†] it is bluish grey, almost white in color and is malleable and ductile; one of the most striking physical properties that it possesses is that of magnetism. Pure iron loses its magnetism as soon as a magnet, which has been placed in its neighborhood, is removed, steel, however, is able to retain the property. Pure iron is not attacked by dry oxygen at ordinary temperatures, when exposed to moist air it undergoes slow oxidation, forming *ferric oxide*, Fe_2O_3; if it is heated in oxygen it burns, forming Fe_3O_4, mixed with Fe_2O_3 (See page 21); it unites with the halogenes in the same manner; iron will rust placed when under water which contains dissolved oxygen, this action is accelerated by the presence of acids and retarded by the presence of alkalis.[‡] *Dilute hydrochloric or sulphuric acids* dissolve iron, liberating hydrogen and forming *ferrous* chloride and

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[*] If the cast iron contains a large amount of phosphorus the crucibles (converters) are lined with limestone, the phosphorus is then oxidized and forms calcium phosphate with the limestone.

[†] The melting point of pure iron has been variously given as being 1560°; 1587°; 1600°; 1800°.

[‡] The rusting is also assisted by the presence of salts, especially of ammonium.

ferrous sulphate respectively, (see page 30,); concentrated sulphuric acid, when cold, is without action, when heated with iron it liberates sulphur dioxide and produces *ferric* sulphate (see page 133); *concentrated* nitric acid has the same effect on iron as it has on aluminum (see page 322), the metal does not dissolve but is transferred to the "passive state;" when in this condition it is no longer attacked by the dilute nitric acid nor will it separate copper from a solution of copper sulphate, a reaction which ordinary iron very readily enters into:

$$Cu\,SO_4 + Fe = Fe\,SO_4 + Cu$$ [*]

Several explanations as to the reason of this condition have been offerred. One of these is that the iron becomes covered with a very thin layer of ferrous-ferric oxide, which is insoluble in nitric acid, this theory, however, is without absolute experimental proof.[*] *Dilute nitric acid* dissolves iron, forming *ferrous nitrate*, while a portion of the acid is reduced to ammonium nitrate (see page 198, a).

Cobalt is quite difficult to obtain in a pure state, because its ores always contain iron and nickel, from which latter element the metal is not easy to separate, and copper, bismuth, lead or silver may also be present. The chief points in the separation are; first, the burning away of the sulphur and arsenic present in the ores (see page 229) and secondly, the separation of the copper, bismuth, etc., by means of sulphuretted hydrogen, after the oxides produced by the roasting have been dissolved in acids. The solutions, which remain after the sulphides which have been precipitated have been filtered off, are treated with chlorine and calcium hypochlorite, by this means the cobalt salts, which are present, are oxidized to insoluble cobaltic oxide before those of nickel are attacked, the cobaltic oxide, when the operation has gone just far enough, is separated, dried, and reduced to metallic cobalt by heating in a current of hydrogen.

Nickel is more easily obtained than cobalt, for the reason that it is present in greater quantity and that its ores are, as a rule, purer. The sulphides or arsenides of nickel are roasted in the same manner as those of cobalt, the oxide so obtained is mixed with charcoal and heated, by which means reduction to metallic nickel takes place.

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[*] See page 301, foot note.

[†] In support of this theory is the fact that the passive state can also be produced by other oxidizing agents, such as chloric, bromic, iodic or chromic acids. Another theory of considerable plausibility is that the iron becomes covered with a thin layer of gas, both hypotheses are borne out by the fact that passive iron, when rubbed, returns to its normal state.

Cobalt forms crystalline, metallic plates which have a specific gravity of 8.5 and which melt at a somewhat lower temperature than iron. Like the latter, cobalt is capable of attracting the magnet. The metal is susceptible of a very high polish, is malleable and very ductile. The metal, after it has been cast into solid pieces, is entirely unaltered by the action of the air, but, at white heat, burns to form cobaltous-cobaltic oxide, $Co_3 O_4$. When heated and then plunged into concentrated nitric acid it becomes "passive." Hydrochloric or sulphuric acid slowly dissolve the metal, forming *cobaltous chloride* and *cobaltous sulphate* respectively. Dilute nitric acid readily dissolves cobalt to produce *cobaltous nitrate.*

Nickel.—It is doubtful if chemically pure nickel has ever been obtained (see page 445); that which has hitherto been regarded as such is produced by reduction from the pure oxalate of nickel. When cast into cubes it is a lustrous, almost silver-white metal which is nearly as malleable and ductile as iron. It melts at a temperature lower than the melting-point of either cobalt or iron. It is attracted by the magnet at ordinary temperatures, but loses this property when heated to 350°. Nickel, which has been cast into solid pieces, is not oxidized in the air and it scarcely burns even when heated white hot in an atmosphere of oxygen. The metal is but slowly attacked by hydrochloric or sulphuric acids; it readily dissolves in nitric acid to form nickelous nitrate. Concentrated nitric acid renders the metal "passive." The specific gravity of nickel is 8.9.

Alloys of iron which are of commercial importance are those with zinc and tin, as the covering of iron plates with those metals depends on the formation of alloys. Alloys of manganese, tungsten or nickel, with steel, possess great toughness.

Alloys of nickel are used in the preparation of coins,* in the formation of German silver (which contains copper, zinc and nickel) and in a number of other ways. Nickel plating is accomplished by electrolyzing a solution of nickel-ammonium sulphate,† the metal to be covered being the negative electrode.

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*The nickel coins of the United States contain 75 per cent. copper and 25 per cent nickel.

†Steel can be nickel plated by simply plunging into a bath of nickel-ammonium sulphate.

Compounds of iron:—Iron forms two series of compounds, *ferrous* compounds, in which the metal is divalent, and *ferric* compounds, in which it is trivalent. Besides these two stages of oxidation, there exists a *ferric acid,* (the anhydride of which would be $Fe\ O_3$) in which iron is hexavalent.

Ferrous oxide, $Fe\ O$, is produced by reducing ferric oxide in a current of hydrogen; the corresponding hydroxide is $Fe\ (O\ H)_2$. The latter is precipitated by adding ammonia water to a solution of a *ferrous* salt; the precipitate is white, but rapidly turns brown on exposure to the air, while *ferric hydroxide* is produced. Both ferrous oxide and hydroxide are bases; they dissolve in acids to form ferrous salts.

Ferrous chloride is produced by dissolving iron in hydrochloric, acid while excluding the air. The dry salt, $Fe\ Cl_2$, can then be isolated by evaporating the solution in a current of hydrogen. It is a white, crystalline mass which volatilizes at a high red heat. The vapor density of ferrous chloride, at white heat, air = 1, is 4.39. This number corresponds to a molecular weight given by the formula $Fe\ Cl_2$. At a lower temperature the molecules are probably $Fe_2\ Cl_4$. When exposed to the air, ferrous chloride rapidly oxidizes to a mixture of ferric chloride and ferric oxide:

$$6\ Fe\ Cl_2 + 3\ O = 4\ Fe\ Cl_3 + Fe_2\ O_3.$$

When in solution, *provided hydrochloric acid is present,* ferric chloride alone is produced:

$$2\ Fe\ Cl_2 + 2\ H\ Cl + O = 2\ Fe\ Cl_3 + H_2\ O.$$

On the other hand, if an excess of hydrochloric acid is not present, ferric chloride and an insoluble basic ferrous chloride are formed:

$$4\ Fe\ Cl_2 + H_2\ O + O = 2\ Fe\left\{\begin{matrix}O\ H\\ Cl\end{matrix}\right. + 2\ Fe\ Cl_3.$$

Of course, the usual oxidizing agents (nitric acid, potassium chlorate and hydrochloric acid, chlorine, bromine, etc.) instantly change ferrous chloride into ferric chloride. Ferrous chloride, like the chlorides of the majority of other divalent elements, forms double salts with the chlorides of the alkalis, as well as with the chlorides of a number of other metals.

Ferrous sulphate (green vitriol, copperas), $Fe\ S\ O_4 + 7\ H_2\ O$, is isomorphous with the vitriols (see page 394). It is produced, commercially, by the spontaneous oxidation of iron pyrites, or by dissolving iron in dilute sulphuric acid (see page 30). The salt loses six molecules of water at 100° and is completely dehydrated at 300°; it then forms a white powder. Like the other vitriols, ferrous sulphate forms double salts with the sulphates of the alkali metals; the latter contain six molecules of water of crystallization and have the general formula, $Fe\ S\ O_4$, $M_2\ S\ O_4 + 6\ H_2\ O$; they are not as easily oxidized as the pure sulphate of iron. When exposed to moist air, *ferrous sulphate* is oxidized to a mixture of *ferric sulphate* and ferric hydroxide:*

$$6\ Fe\ S\ O_4 + 3\ H_2\ O + 3\ O = 2\ Fe_2\ (S\ O_4)_3 + 2\ Fe\ (O\ H)_3,$$

while, in the presence of sulphuric acid, *ferric sulphate* alone is produced:

$$2\ Fe\ S\ O_4 + H_2\ S\ O_4 + O = Fe_2\ (S\ O_4)_3 + H_2\ O.$$

The usual laboratory oxidizing agents have the same effect. Ferrous sulphate absorbs nitric oxide ($N\ O$), forming an unstable chemical compound with the latter. The solution is dark brown in color and parts with the dissolved gas when heated.†

Ferrous sulphide, $Fe\ S$, sometimes occurs as a mineral. It is formed by heating together iron and sulphur or by precipitation, as a black powder, when the solution of an alkaline sulphide is added to a solution of a ferrous salt:

$$Fe\ S\ O_4 + (N\ H_4)^2\ S = Fe\ S + (N\ H_4)_2\ S\ O_4.$$

Ferrous sulphide belongs to the class of sulphides which are dissolved by dilute acids; it is, therefore, not precipitated by hydrogen sulphide in acid solution (see page 95). When an alkaline sulphide is added to a solution containing a *ferric* salt, not *ferric sulphide* but *ferrous sulphide*, mixed with sulphur, is precipitated, this phenomenon being due to the instability of ferric sulphide in aqueous solution; the change can be represented by following equations:

1. $Fe_2\ S_3 = 2\ Fe\ S + S.$
2. $Fe_2\ (S\ O_4)_3 + 3\ Na_2\ S = 2\ Fe\ S + S + 3\ Na_2\ S\ O_4.$

Ferrous carbonate, $Fe\ C\ O_3$, occurs as the mineral siderite, isomorphous with calcite. It can be formed in the laboratory by adding a soluble carbonate to a solution containing a ferrous salt:

$$\underset{\text{Soluble.}}{Fe\ S\ O_4} + Na_2\ C\ O_3 = \underset{\text{Soluble.}}{Na_2\ S\ O_4} + \underset{\text{Insoluble.}}{Fe\ C\ O_3}.$$

When moist, ferrous carbonate is readily oxidized by the air, *ferric hydroxide* remaining, for ferric hydroxide (like the hydrox-

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* Possibly a basic sulphate.

† The formation of this solution is a delicate test for nitric acid. Nitric acid oxidizes ferrous sulphate as follows:

$$6\ Fe\ S\ O_4 + 2\ H\ N\ O_3 + 3\ H_2\ S\ O_4 = 3\ Fe_2\ (S\ O_4)_3 + 4\ H_2\ O + 2\ N\ O;$$

the nitric oxide, which is liberated, colors the excess of ferrous sulphate. Of course, this test can also be used for detecting the presence of a *nitrate*, for the latter, with sulphuric acid, forms a sulphate and free nitric acid.

ide of aluminium and chromic hydroxide) is too weakly basic to form a carbonate (see page 329). Ferrous carbonate is easily decomposed into ferrous oxide and carbon dioxide by heat.

Ferric oxide, $Fe_2 O_3$, is found in nature as hematite, in the laboratory it can be produced by heating the corresponding hydroxide, $Fe (OH)_3$:

$$2 Fe (OH)_3 = Fe_2 O_3 + 3 H_2 O;$$

the oxide so prepared has a fine red color; it is known as *rouge* and is used as a polish for metals and glass. *Ferric hydroxide* is precipitated by adding an alkaline hydroxide or ammonia water to a solution containing a ferric salt,

$$Fe_2 (SO_4)_3 + 6 K OH = 2 Fe (OH)_3 + 3 K_2 SO_4;$$

the ferric hydroxide so formed probably loses water spontaneously, so that the precipitate is really the metahydroxide $Fe O (OH)$. A number of the ferric hydroxides, which are formed by the separation of water between two or more formula weights of the normal hydroxide, occur as minerals which are commercially important; such compounds are limonite, $(4 Fe (OH)_3 = Fe_4 O_3 (OH)_6) + 3 H_2 O$ and xanthosiderite (bog iron ore) $Fe_2 O (OH_4)$,* the latter isomorphous with beauxite (see page 321). Ferric hydroxide can also be obtained, in a soluble form, by dialyzing an extremely dilute solution of ferric chloride mixed with ammonium carbonate (see pages 294, 295), the solution has properties similar to those of dialyzed silicic acid. Ferric hydroxide is distinguished from the hydroxide of aluminium and from chromic hydroxide by the fact that it is insoluble in an excess of caustic alkali, nevertheless, it *does* possess acidic properties, as is proved by the existence of minerals like *franklinite*, for the latter is a *zinc ferrite*, $Zn (Fe O_2)_2$ derived from meta ferric hydroxide $Fe O (OH)$†; franklinite is isomorphous with spinell (see page 321) the latter being a salt of meta aluminum hydroxide, $Al O (OH)$, acting as an acid. Besides being acquainted with zinc ferrite, we know that magnetite is in all probability a ferrous salt of ferric hydroxide, for it has the formula $Fe (Fe O_2)_2$ and is isomorphous with spinell, and lastly, calcium and barium ferrites can be produced in the laboratory by heating ferric oxide with calcium or barium oxide to a high red heat; the latter salts have the composition:

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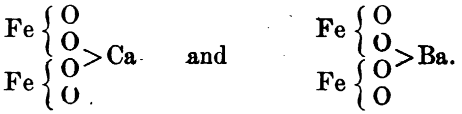
* $2 Fe (OH)_3 = Fe_2 O (OH_4) + H_2 O$.

† In franklinite a part of the zinc is replaced by ferrous iron and by manganous manganese.



$$\begin{array}{l}\mathrm{Fe}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right.\\ \mathrm{Fe}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right.\end{array}\!>\mathrm{Ca} \quad \text{and} \quad \begin{array}{l}\mathrm{Fe}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right.\\ \mathrm{Fe}\left\{\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right.\end{array}\!>\mathrm{Ba}.$$

On the other hand, ferric oxide and ferric hydroxide are *bases*, for they dissolve in acids to form *ferric* salts.*

Ferric chloride; $Fe\,Cl_3$, can be produced by dissolving ferric hydroxide in hydrochloric acid or by passing chlorine into a solution of ferrous chloride:

$$Fe\,Cl_2 + Cl = Fe\,Cl_3;$$

Upon evaporation in the cold, crystals of the composition $Fe\,Cl_3 + 3\,H_2O$ are deposited, another hydrate of the formula $Fe\,Cl_3 + 6\,H_2O$ is formed if the solution is allowed to stand at ordinary temperatures; a solution of ferric chloride cannot be heated, because, then, it breaks down into hydrochloric acid and an insoluble oxychloride;† reducing agents, such as hydrogen sulphide, zinc and hydrochloric acid, sulphurous acid, etc., change *ferric chloride* into *ferrous chloride.* Anhydrous ferric chloride is prepared by passing chlorine over powdered iron, the chloride evaporates at the temperature of boiling sulphur (448°) and its vapor density, even at that temperature, is too low for a substance consisting of molecules having the formula $Fe_2\,Cl_6$, the specific gravity of the gaseous chloride rapidly decreases as the temperature is raised, so that no doubt can exist as to the trivalence of iron in ferric chloride, the molecule of which, in a gaseous state, is expressed by the formula $Fe\,Cl_3$, (see page 323).‡ Ferric chloride combines with other chlorides to form double salts similar to those produced by aluminium chloride (see page 325).

Ferric sulphate $Fe_2\,(SO_4)_3$ is formed by oxidizing *ferrous sulphate* (see page 445) or by dissolving ferric hydroxide in sulphuric acid, it forms alums with the sulphates of the alkali metals (see page 327).

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* Ferric oxide, like the oxides of aluminum and chromium, is not dissolved by acids after it has been heated to a red heat.

† If the solution is quite dilute, complete decomposition and formation of *soluble ferric hydroxide* takes place:

$$Fe\,Cl_3 + 3\,H_2O = Fe\,(OH)_3 + 3\,H\,Cl.$$

‡ W. Grünewald and V. Meyer, Berichte der Deutsch. Chem. Gesell. 21, 687.

Ferric sulphide, Fe_2S_3, analogous to ferric oxide, Fe_2O_3, can be produced by heating ferrous sulphide and sulphur to a red heat:

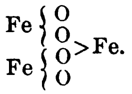
$$2\,FeS + S = Fe_2S_3;$$

it has the character of an acidic anhydride and forms a number of salts which occur as natural minerals, an example of these compounds is chalcopyrite (copper pyrites) in which *cuprous sulphide* is the base:

$$Cu_2S + Fe_2S_3 = Cu_2Fe_2S_4.$$

These sulphoferrites are analogous to the *ferrites*, (examples of the latter occur in the spinell group); when heated, ferric sulphide is converted into the compound Fe_3S_4, this change is similar to that undergone by ferric oxide.

Ferrous-ferric oxide, Fe_3O_4 occurs as *magnetite*, a mineral which has the power of being attracted by the magnet. The oxide is produced when iron is burned in an excess of oxygen, or when steam is passed over red hot iron (see page 30), the black coating which forms on iron which is heated to a high red heat, consists of a mixture of Fe_3O_4 and Fe_2O_3. Ferrous-ferric oxide is considered to be constituted similarly to the spinells, its structure would, therefore, be represented as follows:



$$\begin{array}{l} Fe\left\{\begin{array}{l}O\\O\end{array}\right.\\ Fe\left\{\begin{array}{l}O\\O\end{array}\right.\end{array}\!\!>Fe.$$

The sulphide, Fe_3S_4, which, in formula, corresponds to magnetite, is produced, when a current of the hydrogen sulphide is passed over red hot iron (see page 30):

$$3\,Fe + 4H_2S = Fe_3S_4 + 8\,H.$$

Like the oxide, it has magnetic properties.

Ferric acid is not known in the free state, the *ferrates*, which in formula are analogous to the sulphates, chromates and manganates, however, exist in limited numbers, the best known of these is potassium ferrate, K_2FeO_4; the latter is produced, *just as is potassium manganate*, by fusing the metal with potassium nitrate; the same salt is also formed by passing chlorine into a solution of potassium hydroxide which contains ferric hydroxide in suspension.* Potassium ferrate, as well as the other ferrates, is unstable, when allowed to stand it breaks down, giving off oxygen and leaving ferric hydroxide.

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* The oxidizing agent is the potassium hypochorite which is produced (see page 116), the solution of ferrate of potassium has a violet color. Ordinary potassium hydr-

The disulphide of iron, $Fe\ S_2$, has no analogon among the oxygen compounds of the metal, it is, however, extremely important because it occurs so widely distributed as iron pyrites. The disulphide is dimorphous, as pyrites it crystallizes in the regular system and as markasite it is rhombic, it has a metallic lustre and, on superficial examination, has somewhat the appearance of gold.

The cyanides of iron, the ferro and ferricyanides, as well as the corresponding acids, were discussed on page 285.

Compounds of Cobalt:—Cobalt forms two series of compounds, *cobaltous* compounds, derived from *cobaltous* oxide, $Co\ O$, and *cobaltic* compounds, derived from cobaltic oxide, $Co_2\ O_3$, the cobaltous salts are the ones which are most frequently met with, cobaltic oxide having only very weakly basic properties.

Cobaltous oxide, $Co\ O$, can be prepared by decomposing the corresponding hydroxide, $Co\ (OH)_2$ by heat, air being excluded; the hydroxide is precipitated by adding an excess of caustic alkali to the solution of a cobaltous salt:

$$Co\ (N\ O_3)_2 + 2\ K\ O\ H = Co\ (O\ H)_2 + 2\ K\ N\ O_3.$$

Cobaltous hydroxide is rose colored, the oxide is olive green; both the oxide and hydroxide are strong bases, dissolving in acids to form cobaltous salts.

Cobaltous chloride, $Co\ Cl_2$ can be formed by dissolving the carbonate or hydroxide in hydrochloric acid; when the solution is evaporated crystals of the composition $Co\ Cl_2 + 6\ H_2\ O$ separate, the latter possess a red color; when heated to 100° the salt becomes violet and has the composition $Co\ Cl_2 + H_2\ O$, at 110°-120° it loses all its water of crystallization and is converted into the anhydrous chloride, $Co\ Cl_2$, which is blue; the same rule appertains to all cobalt salts, when hydrated they are red or rose colored, when anhydrous they are blue.*

---

oxide not infrequently contains some ferric hydroxide and the formation of potassium ferrate, with its violet color, is sure to puzzle the student when he is preparing potassium hypochlorite.

* This property of cobalt salts caused the use of those substances as far back as 1757 for the preparation of sympathetic ink; the latter consists of cobalt chloride in solution, it is, therefore, pale red, and almost invisible on the paper When the latter is heated, however, the salt becomes anhydrous and the writing appears in plain, blue characters.

Cobaltous nitrate, $Co(NO_3)_2 + 6\ H_2O$, is the most common cobalt salt, it loses water at 100° and, at a higher temperature, decomposes, giving off NO_2 and leaving *cobaltic* oxide.

A cobalt glass, formed by fusing silicon dioxide, potassium carbonate and some salt of cobalt, has an intensely blue color, when finely ground it is known as smalt, the glass has approximately the same composition as ordinary potash-glass (see page 398) with the exception that the calcium is replaced by cobalt. Fused borax will dissolve cobalt oxide, or salts of cobalt, leaving an intensely blue, glass-like substance which contains cobaltous metaborate, the same is true of sodium metaphosphate, the formation of these two compounds is a ready means for detecting the presence of cobalt. When heated with aluminum oxide, cobalt compounds form a blue cobalt aluminate which is known as Thènard's blue.

Cobaltus sulphide, Co S, is a black precipitate, formed by adding an alkaline sulphide to a solution containing a cobalt salt:

$$Co\ (NO_3)_2 + (NH_4)_2\ S = Co\ S + 2\ NH_4\ NO_3,$$

it differs from ferrous sulphide by not being soluble in dilute acids.

Cobaltic oxide, $Co_2\ O_3$, has very weakly basic properties, its salts, which are formed by dissolving the oxide in cold acids, are easily decomposed, and are tolerably stable only in solution; a number of double salts, derived from a cobaltic salt united with a salt of some other base, are known, these are more stable than the pure cobaltic salts.

Cobaltic nitrite combines with potassium nitrite to form a double salt of the composition $Co\ (NO_2)_3,\ 3\ KNO_2$, the latter is of importance because it is insoluble in water and in cold, dilute acids; its precipitation can, therefore, be used in separating cobalt from nickel; it is produced by adding potassium nitrite to a slightly acid solution of a cobalt salt, the *nitrous* acid, which is liberated from the potassium nitrite, then oxidizes the *cobaltous* compound to a *cobaltic* one, after which reaction, the double nitrite of cobalt and potassium is precipitated.

A solution of *cobaltous chloride*, when in the presence of ammonia* and exposed to the air, is slowly oxidized, by this means there is then formed a peculiar series of compounds composed of *cobaltic* chloride, united with a varying number of molecules of ammonia, these compounds are known as *cobalt amines*, the structural composition of the latter, despite the extended amount of work which has been done upon them, is, as yet, not understood; analysis shows us that one atom of cobalt can unite with 3, 4, 5 and 6 molecules of ammonia to form different radicles which can play the part of individual trivalent bases, these bases, themselves, exist only in aqueous solution, the salts derived from them are, however, stable; the ammonia in these compounds cannot, therefore, be compared to water of crystalization, as it was in the case of the ammonia compounds of copper sulphate (see page 382). Only a few of the simpler connections can be traced here, for a more extended review of this complicated subject the pupil must refer to a larger text-book.[*]

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*The addition of an excess of ammonia to cobaltous salts does not produce a precipitate of hydroxide; the same, it will be remembered, is true of cupric salts.

From solution of $Co\ Cl_2$ in air are produced
1. Dichrocobaltic chloride, $Co\ (N\ H_3)_3\ Cl_3 + H_2\ O$.
2. Praseocobaltic chloride, $Co\ (N\ H_3)_4\ Cl_3 + H_2\ O$.
3. Roseocobaltic chloride, $Co\ (N\ H_3)_5\ Cl_3 + H_2\ O$.
   Purpureocobaltic chloride, $Co\ (N\ H_3)_5\ Cl_3$[†]
4. Luteocobaltic chloride, $Co\ (N\ H_3)_6\ Cl_3$.

The radicles which assume metallic functions in this series of salts can be compared with metallic cobalt, for from each, in addition to the chlorides, a number of other salts, such as the nitrate and sulphate, are derived. The relationship is demonstrated by the following table:

$Co\ Cl_3$, cobaltic chloride;	$Co\ (N\ O_3)_3$, nitrate;	$Co_2\ (S\ O_4)_3$,	sulphate;
$Co\ (N\ H_3)_3\ Cl_3$, dichro salts;	$Co\ (N\ H_3)_3\ (N\ O_3)_3$, nitrate;	$[Co\ (N\ H_3)_3]_2\ (S\ O_4)_3$,	"
$Co\ (N\ H_3)_4\ Cl_3$, praseo salts;	$Co\ (N\ H_3)_4\ (N\ O_3)_3$, nitrate;	$[Co\ (N\ H_3)_4]_2\ (S\ O_4)_3$,	"
$Co\ (N\ H_3)_5\ Cl_3$, roseo salts;	$Co\ (N\ H_3)_5\ (N\ O_3)_3$, nitrate;	$[Co\ (N\ H_3)_5]_2\ (S\ O_4)_3$,	"
$Co\ (N\ H_3)_6\ Cl_3$, luteo salts;	$Co\ (N\ H_3)_6\ (N\ O_3)_3$, nitrate;	$[Co\ (N\ H_3)_6]_2\ (S\ O_4)_3$,	"

The cyanides of cobalt correspond to those of iron (see page 285).

The compounds of nickel are almost exclusively derived from *nickelous oxide*. The latter can readily be produced by heating the hydroxide, $Ni\ (O\ H)_2$, which is precipitated as a grass green substance on adding a soluble hydroxide to a solution containing a salt of nickel.[‡] Nickel salts, when hydrated, are green, when anhydrous, yellow.

Nickelous chloride, $Ni\ Cl_2 + 6\ H_2\ O$, is formed by dissolving the oxide or hydroxide in hydrochloric acid. *Nickelous sulphate*, produced by substituting sulphuric for hydrochloric acid, is isomorphous with the vitriols (see page 394). *Nickelous sulphide* is precipitated as a black powder when a solution of an alkaline sulphide is added to a solution containing a nickelous salt:

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[*] Ladenburg, Handwörterbuch der Chemie; volume 5.

[†] Roseocobaltic chloride is formed from cobaltic chloride and concentrated ammonia in the cold, purpureocobaltic chloride by boiling the same with concentrated hydrochloric acid. The difference is in the water of crystallization.

[‡] Excess of ammonia water dissolves the hydroxide; this is similar to the action of cobaltous hydroxide and cupric hydroxide.

$$\mathrm{Ni\,S\,O_4 + (N\,H_4)_2\,S = Ni\,S + (N\,H_4)_2\,S\,O_4}.$$

Nickelous sulphide is insoluble in dilute acids.

The cyanides of nickel do not correspond to those of iron and cobalt, with the exception of *nickelous cyanide.* The latter, with a formula of $\mathrm{Ni\,(C\,N)_2}$, is precipitated when potassium cyanide is added to a solution containing a salt of nickel, on addition of an excess of the reagent it forms a double cyanide of the formula $\mathrm{Ni\,(C\,N)_2,\ 2\,K\,C\,N}$, which, therefore, does not correspond to the potassium salts of ferrocyanic and of cobaltocyanic acids:

$\mathrm{Ni\,(C\,N)_2,\ 2\,K\,C\,N}$.	$\mathrm{K_4\,Fe\,(C\,N)_6}$.	$\mathrm{K_4\,Co\,(C\,N)_6}$
Double salt of nickel.	Potassium ferrocyanide.	Potassium cobaltocyanide.

Potassium ferrocyanide and cobaltocyanide can be readily oxidized to the cobaltic and ferric compounds, $\mathrm{K_3\,Fe\,(C\,N)_6}$ and $\mathrm{K_3\,Co\,(C\,N)_6}$, which are salts of cobalticyanic acid and ferricyanic acid, but the nickel cyanide is not capable of oxidation. Nickel can be precipitated from its double cyanide by the usual reagents, such as ammonium sulphide, while the iron or cobalt cannot be separated by any such means, when they have entered into the formation of the peculiar acids from which their double cyanides are derived. In the behavior of its cyanides, in the isomorphism of its sulphate with the vitriols and in a number of other respects, nickel resembles the first element in the second half of the long period, namely, copper.

The relationship between the formulæ of the compounds of iron, cobalt, nickel, chromium, manganese and sulphur are given in the following table:

Oxides which are basic and salts derived from them,

ous oxides	*ous* salts.			*ic* oxides.	*ic* salts.		
$\mathrm{Cr\,O}$	$\mathrm{Cr\,Cl_2}$*	$\mathrm{Cr\,SO_4}$*	——	$\mathrm{Cr_2\,O_3}$‡	$\mathrm{Cr\,Cl_3}$	$\mathrm{Cr_2\,(SO_4)_3}$	$\mathrm{Cr\,(NO_3)_3}$
$\mathrm{Mn\,O}$	$\mathrm{Mn\,Cl_2}$	$\mathrm{Mn\,SO_4}$	$\mathrm{Mn\,(NO_3)_2}$	$\mathrm{Mn_2\,O_3}$	$\mathrm{Mn\,Cl_3}$†	$\mathrm{Mn_2(SO_4)_3}$	——
$\mathrm{Fe\,O}$	$\mathrm{Fe\,Cl_2}$	$\mathrm{Fe\,SO_4}$	$\mathrm{Fe\,(NO_3)_2}$	$\mathrm{Fe_2\,O_3}$‡	$\mathrm{Fe\,Cl_3}$	$\mathrm{Fe_2\,(SO_4)_3}$	$\mathrm{Fe\,(NO_3)_3}$
$\mathrm{Co\,O}$	$\mathrm{Co\,Cl_2}$	$\mathrm{Co\,SO_4}$	$\mathrm{Co\,(NO_3)_2}$	$\mathrm{Co_2\,O_3}$	$\mathrm{Co\,Cl_3}$	——	——
$\mathrm{Ni\,O}$	$\mathrm{Ni\,Cl_2}$	$\mathrm{Ni\,SO_4}$	$\mathrm{Ni\,(NO_3)_2}$	$\mathrm{Ni_2\,O_3}$	——	——	——
	chlorides	sulphat's	nitrates		chlorides	sulphates	nitrates.

Compounds marked * are unstable, *very* readily oxidixed; those marked † very readily change to *ous* compounds. $\mathrm{Ni_2\,O_3}$ is known as its hydroxide $\mathrm{Ni\,(OH)_3}$, formed by oxiding a nickelous salt with potassium hypochlorite or hypobromite, it forms no salts.

The *ous* compounds are converted into *ic* compounds by oxidation, the *ic* compounds into *ous* compounds by reduction.

‡ Both basic and acidic, $\mathrm{Cr_2\,O_3}$ dissolves in caustic alkalies to form chromites, $\mathrm{Fe_2\,O_3}$ form some compounds which are analogous to the chromites and aluminates, these salts are derived from a hydroxide $\mathrm{MO\,(OH)}$.

Oxides which are composed of the two given above:

ous-ic oxides.

Cr_3O_4, Mn_3O_4, Fe_3O_4, Co_3O_4.

Of the elements on this table manganese alone forms a dioxide, MnO_2, however, sulphides or arsenides of the the other elements, analogous in structure, are known.

Oxides which are acidic only

a. Acids and salts of the general formula H_2XO_4; type H_2SO_4.

Anhydrides.	Salts.
CrO_3	M_2CrO_4, chromates;
——	M_2MnO_4, manganates;
——	M_2FeO_4, ferrates.

b. Acids and salts of the general formula HXO_4; type $HClO_4$.

Anhydride.	Salts.
Mn_2O_7	$MMnO_4$, permanganates

CHAPTER LX.

THE REMAINING ELEMENTS OF THE EIGHTH FAMILY. (THE PLATINUM GROUP).

Ruthenium, symbol Ru, atomic wt.. 101.6;
Rhodium, symbol Rh, atomic wt., 103.5;
Palladium, symbol Pd, atomic wt., 106.6;
Osmium. symbol Os, atomic wt,, 191.7;
Iridium, symbol Ir, atomic wt., 193.1;
Platinum, symbol Pt, atomic wt., 195.

The six elements named above are all extremely rare and, with the exception of platinum, of little practical importance; they fall into two groups represented by the horizontal lines in the following table, and also into three groups, represented by the vertical columns, as follows:

	Ru,	Rh,	Pd.
atomic weight,	101.6	103.5	106.6
	Os.	Ir.	Pt.
atomic weight,	191.7	193.1	195.

Passing from left to right in each of the two horizontal lines we find a similar gradation in properties as is observed in the group composed of iron, cobalt and nickel, thus, ruthenium and osmium are able to form higher oxides than the remaining four, just as iron was able to form a higher oxide than either cobalt or nickel, and the same distinction in the formulae of the double cyanides which was observed as existing between those of iron and cobalt on the one hand and nickel on the other, is observed between ruthenium, rhodium, osmium, iridium and palladium and platinum; this distinction is made clear by the following table:

$K_4 Fe (CN)_6$	$K_4 Fe (CN)_6$	$Ni (CN)_2, 2 KCN.$
$K_4 Co (CN)_6$	$K_4 Co (CN)_6$	$Pd (CN)_2, 2 KCN.$
$K_4 Ru (CN)_6$	$K_4 Rh (CN)_6$	$Pt (CN)_2, 2 KCN.$
$K_4 Os (CN)_6$	$K_4 Ir (CN)_6$	Pd, Pt.
Ru, Os.	Rh, Ir.	

The difference existing between the oxides can also, perhaps, be best given in the form of a table; the highest oxides belong to ruthenium and osmium; indeed, these are the only two elements which are able to form oxides of the formula MO_4, in which the valence of the element is presumably eight, provided we regard oxygen as having a valence of two. The highest valence toward oxygen *displayed by any element*, therefore, appears in the eighth family; in the following table the formulae of the oxides of the six elements under discussion are compared with those of manganese, the element belonging to the preceding (seventh) family; as will be noticed, there is a great resemblance, although the highest valence of manganese toward oxygen is only seven:

Mn.	Ru and Os.	Rh and Ir.		Pd and Pt.	
	$Ru\,O_4$; $Os\,O_4$	—	—	—	—
$Mn_2\,O_7$	$(Ru_2\,O_7)$*; —	—	—	—	—
$(Mn\,O_3)$†	$(Ru\,O_3)$†; $(Os\,O_8)$†	—	$(Ir\,O_3)$‡	—	—
$Mn\,O_2$	$Ru\,O_2$: $Os\;_2$	$Rh\,O_2$; $Ir\,O_2$		$Pd\,O_2$ $Pt\,O_2$	
$Mn_2\,O_8$	$Ru_2\,O_3$; $Os_2\,O_8$	$Rh_2\,O_3$; $Ir_2\,O_3$		—	—
$Mn\,O$.	$Ru\,O$; $Os\,O$.	$Rh\,O$; $Ir\,O$		$Pd\,O$.	$Pt\,O$.

In the periodic system, the element following palladium is silver, the one following platinum is gold, and, as a consequence, we find considerable resemblance between palladium and silver, (for instance in the formation of the oxide $Pd_2\,O$) and platinum and gold.

The metals of the platinum group all posess a greyish-white color and brilliant metallic lustre, they fuse at a high white heat; the melting points decreasing in the two groups from ruthenium to palladium, and from osmium to platinum; their specific gravities and atomic volumes are as follows:

	Ru.	Rh.	Pd.
spec. grav.	12.61	12.1	11.4
atom. vol.	8.06	8.5	9.3
	Os.	**Ir.**	**Pt.**
spec. grav.	22.4	22.42	21.46
atom. vol.	8.55	8.6	9.08.

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* The anhydride is not known, the salts, the per-ruthenites $M\,Ru\,O_4$, corresponding to the permanganates, are

† The anhydrides are not known, but the salts, manganates, ruthenites and osmites are known, their general formula is $M_2\,X\,O_4$. corresponding to the sulphates. An oxide $Pd_2\,O$ is also known.

‡ One salt, $K_2\,Ir\,O_4$, derived from such an anhydride, has been described.

The elements of the platinum family are, therefore, at the minimum of the curves of atomic volumes belonging to their respective periods, the next following elements, with larger atomic weights, have larger atomic volumes; the platinum metals, therefore, like iron, cobalt and nickel, are malleable and ductile and form colored salts. All of the elements which have small atomic volumes and high specific gravities, display several oxides and series of compounds, in none of these, however, is the chemical character of any such element with small atomic volume so pronounced as to overshadow the character of the other elements in combination; as has been previously remarked, therefore, the crowding of a large amount of matter into a small space seems to be unfavorable for manifestation of very decided metallic or not metallic properties. All of the elements belonging to the eighth family possess the power of condensing and transmitting hydrogen (see page 32).

The members of the platinum family all occur as the uncombined metals, they are never, however, pure, in their natural condition; platinum may be found with only a slight admixture of iron but, as a general rule, alloys of the various metals forming the platinum group, which may also contain silver and gold, occur.

The metals of this group are very difficultly soluble in acids; ruthenium and iridium are not dissolved by any acid; platinum is only attacked by aqua regia; osmium is dissolved by nitric acid as well, while palladium is soluble both in nitric and hydrochloric acid; all of the elements are very easily reduced and isolated from their oxides or halides, they all manifest a great tendency to unite with chlorine. In their chlorine compounds, ruthenium, rhodium and palladium resemble iron, cobalt and nickel, for they form chlorides with the formulæ $M\,Cl_2$ and $M\,Cl_3$; on the other hand, osmium, iridium and platinum have their most stable chlorides derived from a tetravalent metal, with the general formula $M\,Cl_4$, the latter compounds have a great tendency to produce double salts with the chlorides of the alkali metals, these chlorides have the composition $M_2\,R\,Cl_6$,* and can be regarded as derived from an acid $H_2\,R\,Cl_6$, in which $R\,Cl_4$ acts an acidic anhydride, the structure of these acids would, therefore, be analogous to that of fluosilicic acid (see page 291).

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* M represents a univalent alkali metal, R either osmium, iridium or platinum.

The higher oxides of this group (mentioned in the table, page 463) are acidic in their character, the lower ones are, at best, weakly basic. The two tetroxides, $Ru\,O_4$ and $Os\,O_4$* are quite volatile, and are produced by powerful oxidation of the respective metals, they have a most peculiar, penetrating odor which has been compared to that of ozone; † the vapor densities corresponds to molecules of the formula $R\,O_4$.

Derived from a next lower, hypothetical, oxide, in which ruthenium would be heptavalent, we have one salt, $K\,Ru\,O_4$; osmium does not furnish a parallel compound; next to this we have salts of two hypothetical acids, $H_2\,Ru\,O_4$ and $H_2\,Os\,O_4$, which correspond to manganic, chromic and sulphuric acids; the anhydrides, were they known, would have the formulæ $Ru\,O_8$ and $Os\,O_3$; the salts are termed ruthenites and osmites; only the potassium salt of ruthenious acid is known, but the potassium, sodium and barium salts of osmous acid have been isolated.

The dioxide, MO_2 is the highest oxide which is common to all of the platinum metals; it is also the most important of the oxides of this group, because the principal salts are derived from it, the *chief chlorides* of this family having the formula $M\,Cl_4$; the dioxide is basic in its character, although that of platinum is also slightly acidic, for it dissolves in concentrated alkalis to form platinates. The only chloride which need be mentioned in detail is that of platinum, its characteristics can serve as a type for of all the rest.

Platinic chloride, $Pt\,Cl_4 + 5\,H_2\,O$, is prepared by adding silver nitrate solution to the substance which is ordinarily termed platinic chloride, but which is, in reality, an acid of the formula $H_2\,Pt\,Cl_6$; the first reaction is as follows:

$$H_2\,Pt\,Cl_6 + 2\,Ag\,NO_3 = Ag_2\,Pt\,Cl_6 + 2\,HNO_3;$$

the siver salt of chlorplatinic acid, which is precipitated, is decomposed by boiling water as follows:

$$Ag_2\,Pt\,Cl_6 = 2\,Ag\,Cl + Pt\,Cl_4;$$

the insoluble silver chloride is filtered and the solution evaporated to crystallization.

Chlorplatinic acid, $H_2\,Pt\,Cl_6 + 6\,H_2\,O$, is obtained by dissolving platinum in aqua regia and cautiously evaporating, it then forms ochre-colored, deliquescent prisms. The chlorplatinates are of importance in chemical analysis, because ammonium and potassium chlorplatinates are nearly insoluble in water, and entirely insoluble in alcohol. Potassium chlorplatinate is precipitated as a yellow, crystalline substance, when potassium chloride, or any other potassium salt, is added to a solution of platinum chloride, its formula is $K_2 Pt Cl_6$, similar results are obtained with ammonium salts; ammonium chlorplatinate, when heated, decomposes entirely, leaving platinum in a very finely divided, spongy condition in which it is known as "spongy platinum"; spongy platinum possesses the power of occluding gases in a marked degree and its use has been mentioned in several of the preceding chapters (see, for instance, the preparation of sulphur trioxide, page 140).* the use of spongy platinum depends on the fact that occluded gases are chemically much more active than they are in the ordinary condition (see page 32). Platinic bromide or iodide form acids similar to chlorplatinic acid; the structure of these acids is similar to that of fluosilicic acid, $H_2 Si F_6$, which is also derived from a tetrahalide, $Si F_4$, so that in these compounds, also, it is best to accept a theory of the divalence of the halogene atoms (see pages 292 and 325).

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* Sometimes called osmic acid.

† The odor is almost exactly like that of chinon.

Platinic chloride is able to unite with ammonia to form platinic-amines in which the chemical behavior of ammonia is identical with that of the same substance in the cobaltamine salts. Platinic chloride forms a number of these compounds, only two of which it is necessary to mention here.

Platinic chloride can unite with *two* molecules of ammonia to form *chlor-platinamine chloride*, which has the formula $Cl_2 Pt (NH_3)_2 Cl_2$; the radicle $Pt (NH_3)_2$ being tetravalent and uniting with four atoms of chlorine, just as one atom of platinum does in platinic chloride:

$Pt Cl_4$, and $Pt (N H_3)_2 Cl_4$,
Platinum chloride, and chlorplatinamine chloride.

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* "Platinized asbestos" is formed by dipping asbestos in platinum chloride solution and then in one of ammonium chloride; ammonium chlorplatinate is thus precipitated on the fibres and can be changed to spongy platinum by heating. Palladium asbestos can be prepared in the same way. "Platinum black" is very finely divided platinum, formed by reducing a solution of platinum chloride, to which potassium hydroxide has been added, by means of alcohol.

However, in the latter compound, *two* atoms of chlorine can be replaced by other acid groups ($-NO_3$ or $= SO_4$) very readily, while the other two are much less reactive, this compound can therefore also be considered as the chloride of a divalent radicle $Cl_2\,Pt\,(NH_3)_2 =$; because of the difficulty with which they are replaced it is supposed that the two latter chlorine atoms are attached to platinum, while the other two are united to nitrogen in the some way as one atom of chlorine is in ammonium chloride. The structure of the ammonium compound is therefore better represented by the following formula:

$$Cl_2\,Pt \left\{ \begin{array}{l} NH_3\,Cl \\ NH_3\,Cl; \end{array} \right.$$

and the nitrate and sulphate by the following:

$$Cl_2\,Pt \left\{ \begin{array}{l} NH_3\,NO_3 \\ NH_3\,NO_3; \end{array} \right. \text{ and } Cl_2\,Pt \left\{ \begin{array}{l} NH_3 \\ NH_3 \end{array} \right. > SO_4;$$

this theory is borne out by the fact that *platinous chloride*, $Pt\,Cl_2$, can form a similar compound with ammonia, with the exception that two chlorine atoms attached to platinum are missing; this compound therefore has the structure:

$$Pt \left\{ \begin{array}{l} NH_3\,Cl \\ NH_3\,Cl. \end{array} \right.$$

The second series of platinic amines has *four* atoms of ammonia for for every one of platinum; the chloride in this series is therefore chlorplatindiamine chloride and has the formula:

$$Cl_2\,Pt \left\{ \begin{array}{l} (NH_3)_2\,Cl \\ (NH_3)_2\,Cl. \end{array} \right.$$

In this compound there exists the divalent radicle $Cl_2\,Pt\,(NH_3)_4 =$, and the similar combination derived from platinous chloride, having two less chlorine atoms, has the formula:

$$Pt \left\{ \begin{array}{l} (NH_3)_2\,Cl \\ (NH_3)_2\,Cl. \end{array} \right.$$

The monoxide, $M\,O$, as well as the dioxide, is common to all the members of the platinum group, it is basic in its character, and from it are derived the *ous* salts.

Platinous chloride has the formula $Pt\,Cl_2$, it is formed by reduction of a solution of platinic chloride by means of sulphur dioxide; like platinum chloride, it readily forms double salts and unites with ammonia.

The commercial uses of the metals of the platinum group are confined chiefly to the preparation of standard weights and measures, and to the manufacture of chemical apparatus. Most of the platinum which occurs in crucibles and other utensils is not pure, it contains as much as 2 per cent. of iridium and, by very reason of this admixture, is more valuable, because less readily attacked by acids. Platinum vessels are extremely useful because of their high melting point, because they are not attacked oxygen and are not dissolved by the ordinary laboratory reagents. In using platinum ware care must be taken not fuse caustic alkalis therein, nor to heat with any metal or easily reducible compound containing a metal, because platinum readily forms alloys. Furthermore, platinum unites with silicon or phosphorus, the compounds so formed being quite brittle; charcoal or coal which contains silicon compounds in the ash, should never be ignited in a crucible of platinum, and the heating of compounds which contain phosphates in the presence of a reducing agent (such as charcoal) should also be avoided. Luminous gas flames render platinum rough and brittle, the same is true of the reducing flame of a Bunsen burner; unless care is taken to remove this roughness *each time* after using* it will ultimately penetrate the crucible, and, after rendering the utensil brittle, will crack it.

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* By rubbing with a little fine sand until smooth.

APPENDIX OF LABORATORY NOTES.

Before entering upon laboratory work the pupil should read and remember the following cautions.

Burns, stains and fire:—Yellow phosphorus should never be handled excepting with a pair of tongs or pinchers, when exposed to the air in a warm room it may take fire spontaneously, if touched by the hand it will take fire; the burns so produced are extremely painful and may become dangerous by reason of phosphorus poisoning. *Sodium and potassium* are kept under naptha, they should *never* be placed in water when the pieces are larger than beans and, in any event, a very small piece should first be tested; sodium which has not a clear and bright surface when cut, should be rejected, in all cases the outer coating of oxide should be cut away before placing the metal in water. *Burns are best treated* by covering the spot with a solution of cocaine in sweet oil and then with an emulsion of lime water, glycerine and sweet oil. *Nitric acid* stains the skin yellow, where concentrated it will cause an ulcer to form; *bromine* stains the skin brown, unless instantly removed it will cause a painful ulcer; *iodine* stains the skin dark violet; *nitrate of silver* black. Of course, every precaution should be taken to keep the above substances from touching the hands or face but, in case of accident, *dilute* sodium carbonate solution, followed by washing with clean water will be best to apply in the case of nitric acid and bromine; a solution of sodium hyposulphite followed by water will remove iodine; cyanide of potassium solution will remove silver stains.[*] *Concentrated sulphuric acid* and *solutions of chromic acid* will attack the skin, not so rapidly, however, as nitric acid; in case of an accident they can often be removed by washing with water or sodium carbonate solution before serious results have followed; *hot sulphuric acid* will *instantly* produce the most painful burns; *any test tube* in which sulphuric acid or anything else is being heated, should be held by a test tube holder *and with its mouth pointing away from the manipulator or from any one standing near. Ether or carbon bisulphide* must not be used on a desk within at least six feet of a burning Bunsen burner, these liquids take fire with the greatest readiness. Matches should be kept in a tin box which is never to be placed in the drawer of the desk, but should always be kept outside.

Inhalation of fumes and gases:—Chemical experiments which will develope poisonous or irritating gases should always be performed under a hood with a good draught.[†] *Chlorine, bromine, phosphorus pentachloride, phosphorus trichloride* attack the mucous membrane of the eyes, throat and nose, continued inhalation will give rise to bronchial inflammation, chlorine or bromine will also cause nausea to ensue; if, by accident, the pupil should take an excessive quantity of chlorine into the lungs the quickest remedy is probably the inhalation of the fumes of alcohol. *The gaseous oxides of nitrogen* are poisonous, they cause violent headache and nausea; phosphine, arsine, stibine are very poisonous, ammonia is quite irritating; work in which these substances are generated or used *must* be done under the hood.* *Sulphuric acid* should not be heated to above 150° unless the apparatus is under the hood. (The acid will break down, partly, into H_2O and SO_2, the vapors of SO_2 are irritating to the lungs). Liquids containing *hydrochloric acid* or *nitric acid* should be evaporated under the hood. *Sulphuretted hydrogen* is poisonous and disagreeable, continued inhalation of even small quantities will cause headache and may have serious results; it is, therefore, imperatively necessary, unless a room is especially provided in which to generate this gas, that all work with hydrogen sulphide should be performed under the hood.

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[*] The teachers *should not* keep cyanide of potassium in a place where it is accessible to any one but themselves. It should be handled under a hood, and should be applied in removing silver stains, *to the hands only* and then be instantly washed off after its work is accomplished.

[†] So urgent is this rule that pupils should be forbidden even to heat test tubes or small evaporating dishes with reagents which will give off fumes of hydrochloric acid. nitric acid, hydrogen sulphide, bromine, chlorine, nitric oxide, etc., unless they do so under the hood. A good hood is as necessary as a good burner.

Explosions:—The majority of accidents result from carelessness, therefore the invariable rule by which the student should govern himself in the laboratory is, "never be careless, for carelessness may result in permanent disfigurement or loss of sight." *Hydrogen and oxygen, hydrogen and air, hydrogen and chlorine, gaseous hydrocarbons and oxygen, phosphine and oxygen or phosphine and air as well as the other not very stable hydrogen compounds of the not metals when mixed with oxygen or air* will, unless one or the other constituents is present in proportionally small quantity, cause violent explosions when ignited. In generating the gases, extreme care must be taken not to bring a flame near the exit-tube of the apparatus until the pupil is *sure* that a *brisk* current of the generated gas has traversed the apparatus for sufficient length of time to expel all air; of course, no definite time rule can be established, because this will vary with the size of the apparatus, but, when using the ordinary generating flasks of from 300 to 500 c.c. the pupil should wait at least 7 to 10 minutes. *Chlorate of potassium, permanganate of potassium* and similar powerful oxidizers must *not* be rubbed in a mortar when in contact with substances which are readily oxidized (sugar, starch, sulphide of antimony, sulphur, phosphorus, [yellow or red] etc.)

In a well conducted laboratory, desks and apparatus must always be kept as clean as possible and *reagent bottles returned* to their proper places as soon as the occasion requiring their use is over. Bunsen burners can be cleaned by unscrewing the outer tube and brushing the nipple with a dry, stiff test tube brush.†

THE NUMBERS OF THESE NOTES CORRESPOND TO THE REFERENCE NUMBERS IN THE TEXT.

1. PREPARATION OF OXYGEN BY HEATING MERCURIC OXIDE:—The oxide decomposes at a low red heat, a little should be placed in a glass tube 300 m. m. in length, closed at one end and made of so-called infusible glass, outside of the tube place a cylinder of copper wire gauze to prevent cracking; a tripple gas burner is most convenient for heating. The tube is connected with the trough of water, over which the gas is collected, by means of a safety bottle; the latter consisting of an empty 8 oz. wide-mouthed bottle, fitted with a double bored *rubber*

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* In the case of ammonia the precaution may be omitted if only *small* quantities of the reagent are to be used.

† Any instruction in glass bending or blowing which is necessary should be given by the teacher before beginning laboratory work—after the instruction, practice alone will make perfect. The pupil should buy W. A. Shenstone; Methods of Glass Blowing, Rivington's London, 1886.

stopper and connecting glass tubes, the ends of which must *not* extend below the bottom of the stopper. If such a safety bottle is present the water in the trough cannot be forced back into the hot tube, if, by any accident, the flame should be extinguished, for the cold water connot get beyond the safety bottle; if it were to strike the hot tube, an accident would be sure to follow. Such a safety bottle should always be interposed where at pneumaic trough is used to collect gases which are generated in an apparatus which is to be heated to a high temperature. (In the apparatus depicted the place of a tripple burner is supplied by a "combustion furnace." which is a long oven heated by a number of flames) Fig 1.

2. As BLACK OXIDE OF MANGANESE is sometimes adulterated with charcoal, it is always necessary to test the chemical by heating a very little of it in a test tube before using a larger quantity, if no explosion results, it is safe to use.

3. PREPARATION OF OXYGEN BY HEATING MANGANESE DIOXIDE:—The apparatus to be used is identical with that used in the experiment (note 1), *however, an iron tube,* made of ordinary gas pipe, capped and 18 inches in length, is substituted for the glass one. Fill this tube ¼ full of manganese dioxide, broken to the size of a pea.[*] Place the tube flat upon the desk and pound sharply after filling, this is for the purpose of making a canal for the passage of the gas above the load in the tube.[†] Heat to a red heat and *use a safety bottle* (Note 1).

4. THE CHLORATE OF POTASSIUM should be tested in the same way as the black oxide of manganese (Note 2).

5. PREPARATION OF OXYGEN BY HEATING CHLORATE OF POTASSIUM:—Take a flask of 200^{cc} capacity, [‡] fitted with a single bored rubber stopper and glass delivery tube (Fig 2) aud heat to a low red heat, collecting the gas over water in a pneumatic trough; it is best to insert a safety bottle between the generating flask and the water (Note 1). As the flask in which this operation has been performed is always incapacitated for future use, and as the operation is not used for the practical preparation of oxygen, it is better to substitute the following:—heat chlorate of potassium in a hard glass test tube until all of the oxygen is expelled, prove that oxygen is present by placing a glowing pine chip in the tube. The most approved method of preparing oxygen for laboratory use is by heating *a mixture of chlorate of potassium and manganese dioxide.* Mix, in a mortar, 25 grams of potassium chlorate and 5 grams of manganese dioxide, place the mixture in a flask like the one indicated in the first part of this note and shown by Fig 2; heat gently with a Bunsen burner until the gas comes off slowly and regularly, collect all of the gas in bottles over [§] water in the pneumatic trough, and save for future use.

6. COMBUSTION IN OXYGEN:—Burn the substances mentioned in the text, cutting phosphorus, sulphur and carbon to the size of a pea. The deflagrating spoon in which these substances are burned (Fig 3) should

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[*] If this cannot be procured take powdered maganese dioxile.

[†] This precaution must *never* be omitted in charging tubes with solid substances which are to generate gases on heating, otherwise the apparatus will certainly explode.

[‡] Round bottomed flasks made of hard bohemian glass have lately been brought into the market. they are in every way more desirable than flat-bottomed (Erlenmeyer) flasks like that depicted in the cut.

[§] 32 oz. wide mouthed (so-called salt mouth) common bottles are cheapest and best for collecting gases. The pupil should have a number of square pieces of window glass larger than the mouth of the bottle; when necessary to remove the latter, filled with gas, from the trough, cover the mouth with one of the pieces of glass, by pressing the same against the mouth of the bottle. raise the bottle up and invert it, still covered with the glass.

have its handle thrust through a piece of sheet zinc larger than the mouth of the jar containing the gas and pierced with a small hole in the centre. It is well to perform the burning of phosphorus in a large globe, care being taken to have the deflagrating spoon sink so far into the vessel as to reach the center, if the jar is too small the heat is apt to crack it.

7. THE STEEL WATCH SPRING should be heated in the Bunser burner and then straightened, a small piece of cotton is now tied at one end and dipped into molten sulphur; on igniting the sulphur and plunging the spring into a jar of oxygen, the heat given off by the burning sulphur will cause the iron to take fire. A cheap jar should be employed because, during the combustion, the temperature rises high enough to melt the oxide of iron, the small particles of the latter fly off and become fused into the walls or the vessel and may even break it. *To illustrate the kindling temperature,* place a few drops of dry carbon bisulphide in a test tube, warm until the tube becomes filled with the vapors of the liquid and then place the end of a glass rod, which has previously been warmed in a Bunsen burner, within the mouth of the test tube; the carbon bisulphide will take fire, thus furnishing an illustration of a low kindling temperature; the pupil can find examples of high kindling temperature without suggestion.

8. PREPARATION OF HYDROGEN BY MEANS OF SODIUM AND WATER:—The method of preparation is described on page 28 of the text, and the arrangement of the apparatus is made clear by figure 6. If no wire spoon is at hand, the piece of sodium, which should be cut to about the size of a bean, can be wrapped in a small piece of copper gauze, * the latter taken up by a pair of crucible tongs and slid under the mouth of the test tube *which has previously been filled with water and inverted* in the trough; care should be taken to test the sodium to be used in any of these experiments by placing a small piece on water and then standing aside, for, unless the metal is clean, there is great danger of an explosion. Scraps of sodium which have been kept in the laboratory for some time should never be used.

9. This method is expensive and not to be recommended for ordinary purposes. It has been used, however, where perfectly pure hydrogen is requred.

10. THE DECOMPOSITION OF WATER BY POTASSIUM:—The piece of potassium to be used should be cut about the size of a pea, (handle neither potassium nor sodium with the fingers!) and thrown on the water in the pneumatic trough. The decomposition of water by potassium is so violent that the heat generated sets fire to the hydrogen evolved, the latter burning with a violet flame. Care must be taken to stand at some distance from the water on which the potassium is floating, as an explosion may occur by means of which the pieces of the metal will be thrown about, *such pieces can cause painful burns and*, if in contact with the eyes, *possible loss of sight.*

11. GRANULATED ZINC:—Prepared by fusing zinc in a stone ware crucible and pouring the melted metal in a thin stream into cold water, care being taken to *vigorously stir the water* during the operation.

12. TO PREPARE HYDROGEN BY MEANS OF ZINC AND DILUTE SULPHURIC ACID:†—Place 5 grams of zinc in a gas generating flask fitted

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* Filter paper will even answer the purpose. If copper gauze is used, the sodium and gauze will sink to the bottom, the sodium will melt after a time, and, escaping through the meshes of the gauze, will rise; care must be taken to place the tube so as to catch the particles of metal as they rise. If paper is used, the sodium and paper will rise to the top of the tube, and the generation of hydrogen will go on at the point.

† Be sure to use zinc which is free from arsenic or which, at best, contains only a trace of that element.

with a double bored rubber stopper and delivery and safety tube, (Figure 7);* now pour dilute sulphuric acid through the safety tube onto the zinc, adding acid from time to time as occasion requires· *Dilute sulphuric acid* is prepared by adding one part of commercial acid to 6 parts of water; in diluting sulphuric acid, pour the acid, gradually, *into the water*, but do not pour the water into the acid; cool the acid before using, by placing the flask under the hydrant.

13. IN ORDER TO PURIFY THE HYDROGEN prepared as in note 12, it should be passed through a train of wash bottles (Fig. 8). In the first one is placed a solution of potassium hydroxide, (to remove acid vapors), in the second one, a solution of potassium permanganate, (to remove gases which can be oxidized, viz.: hydrocarbons, hydrogen sulphide, hydrogen arsenide, etc.), in the the third one, concentrated sulphuric acid, (to remove moisture). Such a train of bottles can be applied wherever it is necessary to purify a gas, provided, always, the substances used in them are varied according to the nature of the latter, so that no decomposition of the gas can result. A judicious choice of these washing agents comes with larger experience.

14. WHEN LARGER QUANTITIES OF GAS ARE REQUIRED it is better to use a form of gas generator depicted in Fig. 9. A vessel *b*, *d*, constricted in the middle, is fitted with a glass stopcock delivery tube, *e*, and a wide globe funnel, with long stem, is placed in the upper opening. The zinc is placed in *b*, and the acid added from above until the apparatus is filled to about the middle of the funnel; on opening the stopcock the acid ascends to the metal, in closing, the generated hydrogen once more expels it from the central globe. In this way the metals can be kept indefinitely out of contact with the acid, and need only be acted on thereby when the stopcock *c* is opened; this form of gas generating apparatus is known as Kipp's gas generator. Several other forms have been devised, but this one seems to be the most satisfactory, it is useful for generating any gas which does not require heat in its manufacture. Never pour hot acid into a Kipp generator nor never pick it up otherwise than grasping it with *both hands around the central globe.*

Gases which are desired for future use are stored in a gasometer, (Fig. 10). A lower metal tank, holding about forty liters, is connected with an upper one by means of two tubes one of which reaches to the bottom. The gasometer is filled with water, all stopcocks closed, the cap covering the bottom opening is removed, and the gas to be stored is run in through this; when all the water has been replaced, the cap is screwed on. When the gas is to be used, the upper tank is filled with water, the stopcock, on the tube leading to the bottom, is opened, and the gas allowed to escape through the upper, side opening, as required.

15. EFFUSION OF HYDROGEN THROUGH A POROUS SUBSTANCE:—Construct an apparatus such as is shown in Fig. 12, page 55; this consists of a clean dry porous cup † which is fastened at the end of the tube *c* by means of a funnel; this funnel has exactly the diameter of the mouth of the cup and the two are fastened together, *air-tight*, by means of rubber cement placed around the rims. The tube *c* is connected with one opening of a double necked flask ‡ by means of a single bored rubber stopper, while a glass tube, drawn to a point and reaching to the bottom of the flask, is connected with the other opening, also by means

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* A thick walled flask of 300 cc. capacity can be used for this and subsequent operations by which a gas is generated *when there is no necessity of heating the flask.*

† A small porous cup from a Bunsen battery.

‡ So-called Woulff's bottle.

of a rubber stopper; when all the connections are air-tight, place the porous cup in an atmosphere of hydrogen, by inverting a glass bell, open at one end and connected with a hydrogen generator, over the same; the hydrogen will rush through the porous cup much more rapidly than the air can escape, for the specific gravity of air is 14.4 times that of hydrogen. As a consequence, the air in the cup and in c is forced down as if by a piston, this causes a pressure on the water* which has previously been placed in the flask, and a fountain ensues. For an apparatus to illustrate effusion quantitatively see, Freer, Zeitschrift für Physikalische Chemie IX, 669.

16. OCCLUSION OF HYDROGEN:—Palladium is very expensive, one gram will suffice to show occlusion of hydrogen. Attach the palladium to a platinum wire, heat red hot in a Bunsen burner, allow to cool slightly, and then place in a current of hydrogen passing from a generator,† the occluded hydrogen will be oxidized by the air, the palladium will once more begin to glow, and will finally heat the hydrogen to its kindling temperature. So called platinized asbestos is cheaper and just as available for this experiment; prepare platinized asbestos by heating asbestos, which has been dipped in a solution of platinum chloride and then into ammonuim chloride; a little of this can be fastened, by means of fine platinum wire, within a small loop made of iron wire to which a handle about 4 inches in length is attached. Be sure to perform the simple experiment given on the bottom of page 32 and the last one on the first paragraph of the same page.

17. TO PROVE THAT HYDROGEN FORMS WATER WHEN BURNED IN THE AIR:—Dry the gas passing from the generator by means of the train (Note 13) or by passing it through a glass U tube filled with coarse fragments of brick soaked with concentrated sulphuric acid or through a similar tube filled with fragments ‡ of granulated calcium chloride (Fig 14).

18. Care should be taken to expel *all of the air from the apparatus before lighting*, to find out if this has been accomplished, *test the gas by* collecting a test-tube full over water in a pneumatic trough, and lighting this, if it burns quietly, the apparatus is safe. The burner can be made by drawing a glass tube nearly to a point, inserting a small cylinder of rolled platinum foil in the small end so produced, and then fusing the glass around the platinum; after the hydrogen burner has been lighted, place a cold beaker over the flame, and water will collect therein.

19. AN EXPLOSIVE MIXTURE OF HYDROGEN AND OXYGEN.—This can be prepared with safety by using a small bottle, without a bottom and with a narrow neck, to the latter, by means of a single bored rubber stopper and short glass tube, a long rubber tube is fitted. This tube can be closed by means of a pinchcock. The bottle, after the rubber tube is closed by the pinchcock, is filled with water in the pneumatic trough and then hydrogen is run in until $\frac{2}{3}$ of the water has been expelled, the remaining $\frac{1}{3}$ is then similarly replaced by oxygen; the mixture of gases can be expelled by lowering the bottle in the pneumatic trough and opening the pinchcock. By placing the end of the rubber delivery tube under some soap-suds in a small tin dish, a few soap-bubbles filled with oxy-hydrogen can be produced, and then exploded by touching with a lighted taper. *Care should be taken to remove this dish to a safe distance from the bottle before exploding,*

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* For lecture room demonstrations, color the water with blue litmus.

† Take care to have all of the air expelled from the generator!

‡ The size of a pea.

and whatever oxy-hydrogen is left, should be allowed to escape as soon as the experiment requiring its use has been completed. If possible, the experiments with the oxy-hydrogen blow-pipe (Page 34), (Fig 11), should be performed.

20. THE VOLUMETRIC COMPOSITION OF WATER:—Use a eudiometer holding 50^{cc}. This instrument is a glass tube (Fig 13) which is closed at one end and graduated in millimeters (sometimes in cubic centimeters) and has two platinum wires inserted near the closed tip in such a manner that an electric spark can pass from one to the other. * This tube is filled with mercury and inverted over a mercury trough. In order to prove the volumetric composition of water, slant the tube to one side and admit about 10^{cc} of hydrogen, then add 7^{cc} of of oxygen, clamp the tube tightly with its open end forced against a leather washer in the bottom of the mercury trough. taking care to note the exact volume of hydrogen admitted, the volume of oxygen, the temperature, barometer and height of the mercury in the tube. After all of these preparations are completed a spark from an induction coil is passed through the gas. After the explosion is completed † and the apparatus has cooled, note the volume of gas remaining, the temperature and the barometric pressure, as well as the height of the column of mercury in the tube. Reduce the gas before and after explosion to standard conditions by means of the formula on page 168, remembering that the height of the column of mercury in the tube before and after explosion, must be deducted from the barometric pressure. If the pupil used 10^{cc} of hydrogen and 7^{cc} of oxygen, then the 10*cc* of hydrogen will have united with 5*cc* of oxygen to form water, and 2*cc* of oxygen will remain. *The decomposition of water by the electric current* is made clear by Fig 4. The two electrodes are pieces of platinum foil, the water to be decomposed is acidulated with sulphuric acid.

21. THE COMPOSITION OF WATER BY WEIGHT:—Dumas passed hydrogen through a series of U tubes (Fig 14) filled as follows, counting from his hydrogen generator (respectively gasometer).—

U tube No. 1; glass fragments moistened with lead nitrate solution, to remove hydrogen sulphide.
U tube No. 2; glass fragments moistened with silver sulphate solution. to remove hydrogen arsenide.
U tube No. 3; pumice stone moistened with caustic potash solution, to remove carbon dioxide, and other acids, such as sulphurous acid, hydrochloric acid. etc.
U tube No. 4, 5; pieces of solid caustic potash; to remove acids.
U tube No. 6. 7, 8; phosphoric anhydride, to remove moisture.

The last tube he weighed before and after the operation, if it had changed in weight at all, the experiment was rejected, as the hydrogen was not pure. The hydrogen so purified was passed through a tube of hard glass, containing copper oxide, this tube was evacuated by an air pump before beginning the operation, and weighed carefully, it was then connected on one end with the apparatus delivering hydrogen, purified as above, on the other with two U tubes filled with phosphorus pentoxide, the last two were carefully weighed before the operation. The hydrogen was now passed over the copper oxide in the tube which was heated in a combustion furnace (Fig 1) until the oxide was reduced to metallic copper, after the tube had then completely cooled, it was once more evacuated and weighed; the loss in weight was equal to the weight of oxygen used to form water; the two phosphorus pentoxide tubes which were placed after the copper oxide, were also weighed, the *gain in*

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* Not infrequently the eudiometers come to the laboratory with the wires so close together that the spark will not be large enough to ignite the gases, if such is the case, force the ends apart with a long glass rod.

† Wrap a towel around the eudiometer tube before exploding.

weight was equal to the amount of water which had been formed. The pupil should perform this operation with a simpler apparatus, which can consist of the train of wash bottles (Note 13) filled, counting from the hydrogen generator, No. 1, with potassium permanganate solution. No. 2 with lead nitrate solution, No. 3 with caustic potash solution* and lastly a U tube filled with pieces of brick soaked in sulphuric acid; the copper oxide tube should be of hard glass, with a bulb blown on the middle and one end drawn to a narrow opening, to this end, after filling the bulb with granulated copper oxide and weighing the tube on the balance, (weigh to $\frac{1}{10}$ of a milligramme) attach a U tube filled with pieces of brick soaked in sulphuric acid; (weigh this tube also to $\frac{1}{10}$ of a milligram;) now pass the hydrogen through the apparatus, while heating the copper oxide to a low red heat, after reduction is complete, continue to pass hydrogen for some time, so that every trace of water is carried over into the last U tube; allow to cool, weigh and calculate the results as given on page 38; unless the ratio is within $\frac{1}{10}$ of a unit of the proportion 1:8, the experiment should be repeated. The connections between the various parts of the apparatus are made by means of rubber tubing, be sure to have this small enough to fit *air tight* over the ends of the tubes, and make the connections as *short as possible.*

TO PROVE THE PRESENCE OF WATER OF CRYSTALLIZATION; heat a crystal of copper sulphate in a test tube, and see if water passes off, whether at a high or low temperature; next dissolve the anhydrous salt in water, evaporate in a porcelain dish on a water bath † until crystallization begins, set aside to cool and observe the form of the crystals. Note the change in temperature caused by dissolving sodium nitrate in water, and by dissolving fused calcium chloride in water: take a small piece of quick lime and place it in a porcelain dish, then pour on a little water and note the change in temperature. *See pages 41, 42.* An example of an efflorescent salt can be obtained by procuring a few "soda crystals," ($Na_2CO_3 + 10\ H_2O$), a deliquescent substance is fused calcium chloride.

22. PREPARATION OF OZONE:—The apparatus, Fig 5, page 31, is the one generally employed for obtaining considerable quantities of ozone. An outer coating *a* is of tin foil, surrounding a glass tube, an inner glass tube (*c*) is surrounded with thin copper foil, the two are fused together at *b* so that *c* is within *a* and reaches nearly to the end of the latter farthest from *b*. Dry oxygen is admitted to the space between *a* and *c* by the tube *d*, it passes out at *e*: *a* is connected by means of a metal strip with one pole of an induction coil, *c*, by means of a similar metal strip placed at *b* with the other pole, when a current passes, a silent discharge takes place between the tin foil surrounding *a* and the copper surrounding *c*. This discharge must necessarily traverse the oxygen which is passing in at *d* and out at *e*, and by this means ozone is generated. *The preparation of ozone by the student* can be accomplished by placing a few pieces of phosphorus in a good sized bottle with a wide neck, covering them partly with a very dilute aqueous solution of potassium dichromate and sulphuric acid, warming the whole slightly (to about 24°—about the temperature of a hot room in summer) and

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[*] The wash bottles cannot be filled with very much of the required solutions, otherwise the pressure in the hydrogen generator will not be sufficient to overcome the hydrostatic pressure in the washbottles, the gas would, in consequence, not flow.

[†] A copper basin, hemispherical in shape, with the top formed of concentric, movable, copper rings. This vessel is filled with water and heated with a Bunsen burner, substances to be evaporated are placed in porcelain evaporating dishes upon it. Remember that a flame just sufficiently large to cause the water to boil is just as good for heating purposes as one which will cause violent ebullition; and which will necessitate frequent refilling of the water bath.

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of hydrochloric acid through the safety tube to cover the manganese dioxide, then warm gently with a Bunsen burner; *or* mix in a mortar 50 grams of manganese dioxide, 50 grams of sodium chloride, place in the generating flask, connect all parts of the apparatus and then add 150*c.c.* of sulphuric acid (two parts sulphuric acid to one of water) and warm gently. The pupil should prepare chlorine by both of these methods. Collect the chlorine in dry bottles by displacement of air, as is shown in the cut, Fig 15, and when full, cover the bottles with glass plates and place aside for future use; afterwards pass chlorine into 300*c.c.* of water, until the liquid is saturated with the gas. Form chlorine hydrate crystals as indicated on page 60 (paragraph 2). Into the jars filled with chlorine introduce: *a*, a little powdered antimony; *b*, a few pieces of heated copper foil; *c*, a piece of moist litmus paper; *d*, a piece of filter paper, moistened with turpentine. Try the bleaching power of your chlorine water on a piece of colored calico. Experiments with chlorine must be conducted under a hood!

28. BLEACHING BY MEANS OF CHLORINE:—This can best be shown by passing dry chlorine * through a flask of 1 liter capacity which has been fitted a triple bored rubber stopper, connect one of the glass tubes introduced through this with the chlorine generator, connect the second with a small flask containing water, so that the latter can be boiled when desired, so as to force steam into the apparatus, place a glass tube on the third hole of the tripple bored stopper; the latter is for the escape of the superfluous gases, it can, if desired, be so bent as to open into a small jar containing caustic potash solution. Introduce a piece of colored calico into the 1 liter flask and admit dry chlorine, no bleaching action will be observed; now heat the water in the small flask and force in steam, the calico will then be bleached.

29. PREPARATION OF HYDROCHLORIC ACID:—The apparatus to be used is the same as that for the preparation of chlorine (Fig 15). The generator is charged with 20 grams of sodium chloride, and then 30 grams of sulphuric acid (two parts of acid to one of water) are added through the safety tube, heat very gently and collect two jars of the gas as was done with chlorine, pass the remainder of the gas into a beaker containing water.

Hpdrochloric acid is produced by burning chlorine in an atmosphere of hydrogen:—In a small flask (A, Fig 20) of 150*c.c.* capacity, place 10 grams of powdered manganese dioxide. Fit the flask with a single bored rubber stopper into which is inserted a tube, widened at the center and with its widened part filled with pieces of granulated calcium chloride about the size of a pea; after pouring concentrated hydrochloric acid on the manganese dioxide, put this stopper into the flask, allow the chlorine to escape for a time and then invert a jar *B* of hydrogen over the escaping chlorine, taking care to light the hydrogen just before it reaches the chlorine jet; the chlorine will then burn in the hydrogen which fills the jar. *The reverse*, burning hydrogen in chlorine, can be performed by filling the flask *A* with zinc and dilute sulphuric acid and lengthing and bending the delivery tube, so that it can form a burner which can extend *down* into a jar of chlorine; after hydrogen has expelled all of the air from the apparatus, light the jet and lower the flame into the chlorine jar, it will continue to burn; in both experiments fumes of hydrochloric acid will be observed.

30. HYDROCHLORIC ACID:—Place a strip of moistened blue litmus paper in one of the jars of hydrochloric acid gas; place a lighted taper

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* Dry the chlorine by passing it through a U tube containing pieces of brick saturated with conc. sulphuric acid (Note 21.)

in the other and see if the gas supports combustion. To a little of your solution in a test tube add some iron filings; some pieces of zinc; dilute the solution and taste it; try its effects on blue litmus solution. To some dilute hydrochloric acid, to which you have added a few drops of litmus solution, add a solution of sodium hydroxide, drop by drop from a burette[*] until the *red* color of the litmus just turns into *blue, one drop* of acid will then turn the blue litmus *red,* a drop of sodium hydroxide will turn the color back to blue; the solution is then neutral. If it is evaporated, nothing but sodium chloride will remain; that sodium chloride is formed can be proved by adding sulphuric acid to the crystallized remainder. (Pages 72 and 73.)

31. The electrolysis of hydrochloric acid is described in note 26.

The extreme solubility of hydrochloric acid in water can be shown by an apparatus such as is depicted by Fig 19. The upper flask is well filled with dry hydrochloric acid gas, and is stoppered with a single bored rubber stopper, through the latter there runs a glass tube, drawn to a point and sealed without the flask and narrowed within. The large beaker is filled with blue litmus solution. When all is ready, the sealed point is broken under the water. As the fountain is somewhat slow in starting, a small bulb of water, sealed, can be placed within the flask and, when the apparatus is to be used, can be broken by a quick shake. The water will absorb hydrochloric acid, create a partial vacum and the blue litmus solution will run in.

32 DECOMPOSITION OF HYDROCHLORIC ACID INTO ONE VOLUME OF CHLORINE AND ONE OF HYDROGEN:—The apparatus to be used is shown in Fig 21, Page 120, pure, dry hydrochloric acid gas is introdued through the glass stopcock of the apparatus (which has previously been filled with dry mercury) until one arm of the U shaped tube is about ⅔ full, the mercury being allowed to run off at the lower tap as fast as hydrochloric acid enters through the upper stopcock; when enough gas has been admitted, the upper and lower stopcocks are closed and the mercury placed at the same level in both arms. The hydrochloric acid gas is now under atmospheric pressure, the level of the mercury is therefore marked by a rubber ring. Now, sodium amalgam[†] is poured into the open arm until the latter is quite full, a cork stopper is inserted tightly and then the apparatus is shaken from side to side so that the sodium amalgam comes in contact with the gas; the hydrochloric acid is decomposed after the lapse of about one minute. The gas which remains is now carefully brought back into the arm of the apparatus which it originally occupied, the cork stopper removed, and the mercury run out through the lower tap until on the same level in both arms; it will then be seen that the volume of hydrogen left is exactly ½ of that which was occupied by the hydrochloric acid. Take care to have the apparatus, sodium amalgam and hydrochloric acid *perfectly dry* before beginning the experiment, for sodium amalgam, acting on water, will generate hydrogen.

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[*] A burette is a glass tube about 500 *m.m.* in length, one end of which terminates in a narrow tube, closed with a glass stopcock; a measured quantity of liquid can therefore be run out of this instrument by opening the stop-cock at the bottom.

[†] To prepare sodium amalgam, take 500 grams of *dry* mercury, place in a large clay crucible and cover with an iron dish, now cut 7 grams of *clean* sodium into pieces, the size of a hickory nut and throw these into the crucible; to start the reaction, heat a little mercury in a test tube, raise the cover on the crucible a little and pour in the hot mercury, an instant reaction, accompanied by a flash of light will occur, during this, *stand aside* so as not to inhale fumes of mercury; after all is over, stir the sodium amalgam with an iron wire, place in a wide-mouthed glass stoppered bottle, when cool, and keep for future use. Prepare sodium amalgam under the hood.

33. THE PREPARATION OF BROMINE:—Take a tubulated and glass-stoppered retort (Fig 22, page 121) of 200*c.c.* capacity, place in this 10 grams of manganese dioxide and 20 grams of potassium bromide (these constituents previously mixed in a mortar), clamp the retort to a retort stand, as shown in the figure, and thrust the neck of the retort far into the neck of a receiver of 500*c.c.* capacity, this receiver is cooled by means of a stream of water, the escape of which is provided for by a large funnel, placed under the receiver, and which, preferably, should be connected with a sink. When all is ready, add concentrated sulphuric acid to the manganese dioxide and sodium bromide, put in the glass stopper of the retort and seal the latter tightly by means of a little plaster of paris and water, allow the retort to stand for ten minutes, and then heat gently, the bromine will distill and collect in the receiver. The operation should be performed under the hood! Make a solution of bromine in water and try its bleaching power as you did with chlorine; fill a tube about 500*m.m.* in length, closed at one end, with chlorine water and invert over a beaker-glass which is partly filled with the same liquid, and, after properly supporting the tube, place the whole in the sunlight, do the same with bromine water, placing the apparatus filled with the latter beside that containing chlorine water, and after 24 hours, notice the amount of oxygen separated by each halogene, (see Page 76.)

34. PREPARATION OF HYDROBROMIC ACID:—Take a few particles of sodium or potassium bromide, place the same in a test tube, and warm very gently, note color and odor of the gas which is passed off. Pure hydrobromic acid cannot be prepared in this way. The apparatus for the preparation of hydrobromic acid for laboratory use is shown by Fig 23, Page 125. The flask *A* which has a tube fused into the side of the neck * has a capacity of 300*c.c.*, it is fitted with a single bored rubber stopper into which is inserted a drop funnel; the side tube connects with a glass tube *B* which is about 300*m.m.* in length and which is filled with pieces of brick which have been moistened and rolled in red phosphorus, the upward slant to this tube is necessary to prevent pieces of phosphorus and impure water from being carried over into the retort *c*, the latter is interposed, between the tube *B* and the water which is in the beaker glass, solely to prevent the latter from "sucking back" as soon as the current of hydrobromic acid becomes so feeble that solution of the gas in water takes place so rapidly that the gas, which is being generated, is unable to keep the liquid out of the apparatus. By reason of the interposition of the retort, the water can be forced back no further than that vessel, previded its capacity is greater than the volume of liquid in the breaker. Charge the generating flask *A* with 25 grams of red phosphorus and then add *just barely enough water to cover the latter*,† fill the drop funnel, above, half full of bromine, connect all parts of the apparatus, and allow the bromine to fall on the phosphorus slowly, drop by drop, (care!), each drop of bromine will cause a flash of light and the formation of hydrobromic acid. After all of the water in the flask *A* and the tube *B* has been saturated with hydrobromic acid, the latter will escape into the retort *c* and can be collected in a beaker of water, or, as the dry gas, by downward displacement, as is done with chlorine. White crystals of phosphonium bromide (see Page 209) will ultimately clog the apparatus if too little water is present, this may become so serious as to entirely prevent the flow of gas through *B* in

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* A so-called fractional distilling flask,

† In preparing hydrobromic acid the greatest care must be taken not to add too much water, otherwise the liquid will dissolve the hydrobromic acid as fast as it is generated.

which case an explosion will inevitably result. Prevent this accident by adding a few drops of water to the generator *A* as soon as you see phosphonium bromide crystals forming. Perform the same experiments with the solution of hydrobromic acid as you did with hydrochloric acid. Fill one jar with dry hydrobromic acid gas and invert a jar of chlorine, of the same size, over it; observe the separation of bromine and the rate of diffusion of the gases.

35. PREPARATION OF IODINE:—Perform this operation with the same apparatus and same proportions as you used in the preparation of bromine, you can omit the cooling of the receiver; of course, substitute potassium iodide or sodium iodide for the bromide which you used in note 33.

36. PREPARATION OF HYDROIODIC ACID:—The apparatus is the same as that used for the preparation of hydrobromic acid (Fig 23, page 125) with the exception that the bricks, covered with moist red phosphorus, can be omitted from the tube *B*, as all of the iodine which may pass over from the generating flask *A* will be condensed by the cold glass tube. In charging the apparatus, place 50 grams of *iodine* in the generating flask *A*, add to this 10 grams of water; replace the drop funnel used in the hydrobromic experiment by an ordinary funnel, which can be stoppered by a glass rod thrust into the neck and ground into the tip so as to be water tight; through this funnel, after all the connections of the apparatus are tight, gradually drop red phosphorus which has been stirred with water to a thick paste, upon the iodine. By following these directions the generation of phosphonium iodide, which invariably results if the apparatus is arranged exactly as in the preparation of hydrobromic acid, is avoided. Care must be taken not to add the phosphorus too rapidly, otherwise an explosion would result; the proportions which are most successful for the preparation of hydroiodic acid are; 10 parts of iodine, 5 parts of phosphorus and 2 parts of water.

37. THE PREPARATION OF SULPHUR:—*The formation of sulphur by the action of hydrogen sulphide on sulphur dioxide* The apparatus is shown on page 127, fig 24. The flask *C*, with two lateral tubulures, has 500*c.c.* capacity, in the flask *A* place about 10 grams of copper shavings, stopper with a double bored rubber stopper into which is inserted a safety tube and delivery tube, add 100 grams of concentrated sulphuric acid through the safety tube and connect with *C*, as shown in the cut. The double necked (Woulff) wash bottle *B*, which contains a little water, is connected with a hydrogen sulphide generator. The latter is the same as that used for hydrogen, (Note 12), with the exception that the zinc is replaced by 10 grams of ferrous sulphide; the flask *C* has its mouth emptying in a beaker, containing a solution of potassium hydroxide, the latter is for the purpose of absorbing the excess of gases. When all is ready, connect all parts of the apparatus and heat the copper and sulphuric acid in *A* until the ebullition indicates that the formation of sulphur dioxide has begun, *then remove the flame*; next add dilute sulphuric acid to the ferrous sulphide in the generating flask connected with *B*. The sulphur dioxide and hydrogen sulphide will meet in *c*; *after a time*, small drops of plastic sulphur will collect, the latter soon become of opaque and yellow, changing into ordinary rhombic sulphur.*

38. THE DISTILLATION OF SULPHUR:—Bend a test tube and clamp it to a retort stand, as is shown by Fig 27. Place three or 4 grams of sulphur in the test tube and heat, collect the vapors in a cold beaker of water. Endeavor to observe all of the phenomena mentioned on page

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*It takes very nearly an hour to form a good deposit of sulphur.

89, paragraph 1, and observe the formation of flowers of sulphur on the cold surface of the water.

39. THE CRYSTALLIZATION OF SULPHUR;—*Rhombic sulphur.* Take some dry carbon bisulphide* and place it in a test tube, add roll sulphur to this and stopper, allow to stand until the carbon bisulphide has taken up as much sulphur as it will, now pour the clear solution into a second *clean* test tube, stopper the latter with some cotton and put aside in a quiet place. After a time, fine, transparent crystals of rhombic sulphur will separate. *Monoclinic sulphur:*—Melt 100 grams of sulphur in a flat porcelain evaporating dish and then allow to cool until a crust has formed over the surface, perforate this crust by means of a glass rod before the entire mass becomes solid, and then pour off the sulphur which has not solidified through the hole which has been formed. The bottom of the evaporating dish will be covered with colorless, transparent needles of monoclinic sulphur crystals.

40. THE PREPARATION OF HYDROGEN SULPHIDE:—The apparatus used is the same as that employed to generate hydrogen, (Notes 12 and 37). In the generating flask place 20 grams of ferrous sulphide, broken to about the size of a bean, connect the delivery tnbe with one of your bottles from the train used in drying hydrogen, (this bottle should contain a little water, so as to retain any acid fumes which may pass over); after all connections are made, pour dilute sulphuric acid through the thistle tube. Collect the sulphuretted hydrogen which passes off, as you did with chlorine and hydrobromic acid, by displacement of air, in dry bottles (such as you used for hydrogen and oxygen), after three bottles have been filled in this way, pass the remainder of the gas into a bottle filled with water. Apply a lighted taper to one of the bottles filled with dry gas; place a strip of filter paper which is soaked with a solution of lead acetate in the second; pass chlorine from the small chlorine generator, which you prepared for the experiment in note 29, into the third. Take the solution of hydrogen sulphide which you have prepared and add a little of it to a solution of copper sulphate; to a solution of cadmium nitrate, to a hydrochloric acid solution of arsenic trioxide; to a slightly acid solution of stannous chloride† (See page 95 of the text). Experiments with hydrogen sulphide must be conducted under the hood!

41. THE DECOMPOSITION OF HYDROGEN SULPHIDE BY HEAT:—This decomposition can best be shown by the apparatus depicted in Fig 28, page 134. This consists of a flask of about 1 liter capacity, well stoppered with a double bored rubber stopper, into this, two glass tubes are fitted through which run two pieces of tolerably thick copper wire, the tips of the glass tubes being fused around these wires, the extremities of the copper wires are connected by a platinum wire as shown in the cut. Fill the flask completely with gaseous hydrogen sulphide, insert the stopper, and pass an electric current through the platinum wire by attaching the free ends of the copper wires to the two poles of a battery, (the current should be just sufficient so cause the wire to glow); the hydrogen sulphide will decompose at the line of contact of the hot wire.

The experiments leading to the preparation of the oxygen acids and salts of chlorine, bromine and iodine are made sufficiently clear in the text, and need give no difficulty as the pupil is now able to prepare the halogenes and use them in the formation of the various compounds mentioned in chapters 19 and 20. In performing these experiments he should confine himself to the preparation and reactions of those salts which are formed by adding chlorine, bromine and iodine to solutions of potassium hydroxide, and to the formation of calcium hypochlorite by passing chlorine over slaked lime and to the decomposition of calcium hypochlorite by hydrochloric and sulphuric acids.

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* Dry the carbon bisulphide by shaking it with fused calcium chloride.

† The pupil can select solutions of the salts of other metals and study the solubility in acids and in alkalis of the sulphides so produced.

42. THE PREPARATION OF SULPHUR DIOXIDE:—The apparatus is shown on page 135, Fig. 29. The generating flask should be of 500 c. c. capacity, into this place about twenty grams of copper shavings, connect all parts of the apparatus, add about 100 c. c. of concentrated sulphuric acid through the safety tube and heat by means of a Bunsen burner; when the gas begins to pass off, lower the flame so as to secure a regular evolution. The wash bottle contains concentrated sulphuric acid. Collect three jars of the gas by displacement of air and pass the remaining gas into water. See if the gas will burn or will support combustion, put a moist strip of colored calico into one of the jars, and a small red rose,* which has been moistened into another. To portions of the solution of sulphur dioxide in water add, successively, a dilute alcoholic solution of iodide; a solution of bromine; a solution of ferric chloride; a solution of potassium dichromate. (All of these reagents will illustrate the reducing power of sulphur dioxide).

43. LIQUID SULPHUR DIOXIDE.—The most convenient form in which to use sulphur dioxide in the laboratory is as a liquid. The apparatus shown by Fig. 30, page 137, is placed, with all its stopcocks open, in a dish filled with a mixture of pounded ice and salt† and then a slow current of sulphur dioxide, generated as explained in note 43, is passed through. In order to more perfectly cool the gas it should, after leaving the drying flask, traverse a spiral glass tube which is placed in a jar and cooled with snow and salt. When a sufficient quantity of the gas has been liquified, all of the stopcocks are closed and the apparatus is set aside until wanted. When gaseous sulphur dioxide is required, the stopcock *c* is opened, and a portion of the gas run into the small bulb, *c* is then closed, and by opening *b* the gas can be used without interfering with the liquid in the large bulb.

44. THE MANUFACTURE OF SULPHURIC ACID:—A laboratory apparatus for illustrating the manufacture of sulphuric acid is shown in Fig. 30. A large glass globe (A) of about 5 liters capacity is fitted with a rubber stopper in which five holes are bored. Three small flasks (a, b, c) are connected with this by means of glass tubes extending to the middle of the large one, and through the remaining holes two tubes, also extending to the middle of the large flask, are fitted. SO_2 is generated in *a* by heating copper shavings and sulphuric acid, NO in *b* by means of copper and dilute nitric acid (no heat is required), and steam is supplied, as wanted, by heating water in *c*. Air can be forced in at *d* by connecting the tube with a bellows, and the tube c, connected with a hood, is left as a vent hole for the escape of gases. When NO (nitric oxide) comes in contact with air, it is oxidized to a mixture of NO_2 and N_2O_3, so that, after that change has taken place, we have the gas present which is necessary for the formation of sulphuric acid from sulphurous acid. If very little steam is admitted we can easily see the formation of nitrosyl sulphuric acid, for the large globe becomes covered with frost-like crystals of that substance. If an excess of steam is admitted, these crystals disappear and sulphuric acid is formed, the latter collecting as

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*Roses are best to use for bleaching with sulphur dioxide, many other red flowers bleach very slowly, some not at all.

†In making a freezing mixture, do not spare the salt.

an oily liquid. By varying the amounts of NO, SO_2 air and steam, we can study all of the phases of sulphuric acid manufacture.

Take some concentrated sulphuric acid, and add it to a little cane sugar which you have placed in a test tube, stir the mixture with a glass rod and allow to stand under the hood; add 9.8 grams of concentrated sulphuric acid to 1.8 grams of water, place the liquid in a small flask and surround the latter with crushed ice and salt, crystals of $H_4 SO_5$ will form; warm the $H_4 SO_5$ until melted, and once more add 1.8 grams of water, place in the freezing mixture and crystals of $H_6 SO_6$ will separate; melt the $H_6 SO_6$ which you have made and then gradually add more water and notice if there is any increase of temperature.[*] Add some dilute sulphuric acid to a solution of barium chloride; to a solution of strontium chloride and to two solutions of calcium chloride, the first of which is very dilute, the second tolerably concentrated, and note the result (see page 395).

TO ISOLATE NITROGEN FROM THE ATMOSPHERE:—The apparatus is shown by Fig. 33. Take a bell jar of 3 liters capacity, invert it over a glass basin, or over your pneumatic trough, prepare a float made of a flat cork, on one side of which you have fastened a porcelain crucible cover by forcing the handle firmly into the cork, place this cork, with the crucible cover up, in your pneumatic trough, place a piece of phosphorus the size of a bean on the cover and light the phosphorus with a hot wire (care in handling phosphorus!); now invert the bell jar over the float and slightly raise the stopper at the top, so that the gas within, which necessarily expands very greatly owing to the heat given off by the burning phosphorus, can quietly escape. If this precaution is omitted the air will be forced out at the bottom of the jar in large bubbles, the disturbance may even tip over your phosphorus float. After the violent combustion is over, insert the stopper of the bell jar and allow to cool, water will rise in the jar to take the place of the oxygen which has gone to form phosphorus pentoxide, and also to take the place of the air which has been expelled. To test the gas remaining, add enough water to the pneumatic trough to make the level within and without the bell jar alike, and then introduce a lighted taper.[†]

46. THE COMPOSITION OF ATMOSPHERE:—A crude method of determining the volumetric composition of the atmosphere is by means of the apparatus shown by Fig. 34. Divide a long glass tube, closed at one end, into five equal parts by means of rubber rings. Insert this over a long cylinder with water so that the level without and within is at the first ring, and then clamp the tube in place. Now, fix a piece of phosphorus on a long copper wire, taking care not to touch the phosphorus with the hands, bend the wire as shown in the cut, thrust the phosphorus up into the tube and stand the apparatus aside for two days. The oxygen of the enclosed air will then be entirely absorbed and, by sinking the tube so that the level of the water without and within is the same, the amount of nitrogen in the air can be ascertained. By noting the height of the barometer before and after the experiment and then applying the necessary corrections, quite accurate results can be obtained, but, if such are required, a carefully graduated tube must be substituted for the crudely divided one indicated.

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[*] In this experiment it will be necessory to add *water* to *sulphuric acid*; be sure to hold the flask at a safe distance while pouring in the water, otherwise the heat which is generated might cause the latter to boil and spatter drops of sulphuric acid about.

[†] The sides of the bell jar become coated with a red, amorphous solid during this operation, this substance is a sub-oxide of phosphorus with the probable formula $P_4 O$; it is not red phosphorus, as is generally supposed.

In order to accurately measure the relative amounts of oxygen and nitrogen in the atmosphere the eudiometer (Fig. 13) Note 20 is employed; the instrument should have a capacity of 100 c. c., it is partially filled with mercury and inverted over the mercury trough so that about 25 c. c. of air will remain enclosed; about 14 c. c. of hydrogen are now run in, by slanting the tube and placing the delivery tube of a hydrogen apparatus which is generating pure and dry hydrogen under its mouth; take all of the precautions mentioned in Note 20, and ignite the mixture of gases with an electric spark; be sure to accurately read the volume of air and the volume of hydrogen before the explosion, and also to measure the height of the column of mercury as indicated in Note 20, after the explosion read the volume of remaining gas and reduce to standard conditions, exactly as was done before. The hydrogen will have united with the oxygen to form water, therefore, one-third of the volume by which the mixture of the gases which were enclosed in the eudiometer has diminished, must have been oxygen.*

47. THE PRESENCE OF CARBON DIOXIDE IN THE ATMOSPHERE:—Take one of the train of wash-bottles which was used in drying hydrogen, clean it and fill it with clear lime-water and attach to a Bunsen aspirator which you have fastened to the hydrant† and the suction tube of which is connected with your wash-bottle in such a way that air will be drawn through the apparatus in the same direction as hydrogen is forced through it as indicated in Fig. 8, page 41. The lime-water will soon become turbid, owing to the formation of calcium carbonate; if you use two wash-bottles, each of which contains clear lime-water, then the one into which the air first passes will become turbid, while the second will remain clear. *The presence of moisture in the atmosphere* can be shown by exposing an open beaker, containing concentrated sulphuric acid, to the air; after some days the volume will be observed to have increased, while the acid has become diluted with water.

48. THE PREPARATION OF AMMONIA:—The apparatus for the preparation of ammonia is shown on page 108, Fig. 18. The generating flask is of 500 c. c. capacity, in it are placed 50 grams of ammonium chloride and 100 grams of slaked lime; (prepare slaked lime by slowly pouring water on quick lime until the latter finally crumbles to a powder) connect the generating flask with a double-necked, Woulff's bottle (Note 37), the latter being filled with small pieces of quick lime, which are present for the purpose of drying the gas, collect ammonia over *mercury* or by displacement of air in a jar which is held mouth downward, for ammonia is specifically lighter than air. When all connections are made, add enough water to the mixture of ammonium chloride and slaked lime in the flask to cause the latter to roll into lumps on shaking; now

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* If the temperature and barometer are the same before and after the experiment no correction need be made, excepting that caused by the change in the pressure on the enclosed gas, brought about by the differing height of the column of mercury in the eudiometer, the latter must be carefully noted, 1st, when air alone is in the eudiometer, 2d, when hydrogen has been admitted, 3d, after the explosion. As the air contains an unknown amount of moisture, saturate it with water by admitting a drop of water above the mercury in the eudiometer and *then*, unless temperature and barometric pressure are different after the experiment than they were before, there will be no necessity for paying attention to the amount of water present, for the gases will be saturated with water before and after the experiment, (see page 168).

† A Bunsen glass aspirator is a cheap instrument which aspirates air by using the water pressure of a hydrant: it is indispensable for laboratory work, and should be kept in the desk, ready for use. It is attached by means of rubber tubing and its mechanism will explain itself when the instrument is handled. A more effective, but also more expensive, instrument, is a Chapman brass aspirator, this can also be fastened to the hydrant; both forms of aspirator can be purchased of any instrument dealer.

heat gently, and ammonia will pass off. A better form of apparatus for the preparation of ammonia is shown on page 181, Fig 35, the woulff drying bottle is here replaced by a glass tower (a so-called Fresenius drying tower), at the bottom opening of which the gas enters, at the top, after traversing the intermediate space, filled with pieces of quick lime, it escapes. These drying towers are very convenient for laboratory use and, if possible, should be kept on hand. *Ammonia cannot be dried over calcium chloride,* because it combines with that substance; it is self evident that the gas cannot be dried by sulphuric acid.

49. EYPERIMENTS WITH AMMONIA:—*The combustion of ammonia* can be shown by filling a large test tube with oxygen, then passing in some ammonia gas, so as to *partially* displace the oxygen, and then quickly approaching the mouth of the test tube to a gas flame, a weak explosion will follow.* Pass some of the ammonia, which was generated by the experiment mentioned in Note 48, into water, and with the solution of ammonia so produced perform the following experiments:—Place some ammonia in a beaker glass; add a few drops of blue litmus solution and then carefully add hydrochloric acid from a burette, until the solution is neutral, (see Note 30) pour the liquid in the beaker into an evaporating dish and evaporate to dryness on a water bath (Note 21); heat a little of the salt which separates, on a piece of platinum foil; heat some of the salt with slaked lime and water in a test tube; repeat the same experiments, substituting nitric acid and sulphuric acid for hydrocholoric acid.

The absorption of ammonia by charcoal can be demonstrated by the apparatus shown by Fig. 36. This is a test tube filled with dry ammonia and inverted over a basin of mercury; a small piece of charcoal, which has previously been glowed out in a Bunsen burner, is introduced, and the test tube is then clamped with its mouth under the surface of the mercury; the ammonia will be absorbed and the mercury will rise in the tube.

50. THE SOLUBILITY OF AMMONIA IN WATER: — Use the same apparatus which you employed for demonstrating the solubility of hydrochloric acid (Note Fig. 19), filling the flask with dry ammonia gas by displacement of air.

51. AMMONIUM AMALGAM:—In a narrow cylinder of 225 c. c. capacity place 20 grams of ammonium chloride, add enough water so as to just cover the salt and then pour on sodium amalgam, prepared as indicated in the foot note to note 32, the ammonium amalgam will begin to form at once, and the operation can be hastened by gently stirring with a glass rod.

52. THE PREPARATION OF NITROUS OXIDE:—The apparatus which it is best to use for the preparation of this gas is shown on Page 192, Fig 37. This consists of a retort made of infusible glass, the neck of which is either cut off, or widened so as to admit of a single bored rubber stopper and a delivery tube. In this retort place 10 to 15 grams of crystallized ammonium nitrate† and heat to a temperature *just sufficiently high to cause a regular flow of the gas;* collect over the pneumatic trough by displacement of water. Introduce a lighted taper into a jar filled with nitrous oxide and see whether it burns or supports combustion; repeat the experiments given in Notes 6 and 7, using nitrous oxide instead of oxygen; inhale a little of the gas.

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* Take care to wrap a towel around the test tube before bringing its mouth to the flame.

† Test a little of your ammonium nitrate by heating in a test tube before you proceed to the decomposition of larger quantities of the salt!

53. PREPARATION OF NITRIC OXIDE:—Use the apparatus which served for the preparation of hydrogen (Fig 7, note 12), charge the flask with 20 grams of copper shavings, cover with water and *slowly* add ordinary nitric acid, waiting for the reaction to begin after each addition; after all the brown fumes which are at first developed have disappeared, collect the gas over the pneumatic trough by displacement of water. The generation of nitric oxide is most successful at ordinary temperatures, the amount of nitric oxide given off by the copper and nitric acid diminishes as the temperature increases, while the amount of trioxide and peroxide increases.

54. EXPERIMENTS WITH NITRIC OXIDE:—Take one of the bottles which you have filled with nitric oxide and turn it mouth upward, the brown fumes of the higher oxides of nitrogen will appear where contact with the air takes place; repeat the experiments illustrating combustion which you performed with nitrous oxide and with oxygen and satisfy yourself as to whether nitric oxide supports combustion as readily as either of those two gases; place a few drops of carbon bisulphide in one of your bottles of nitric oxide, after you have removed it from the pneumatic trough and covered its mouth with a piece of glass plate, taking care not to admit any more air than is absolutely necessary while pouring in the carbon bisulphide; now, shake the bottle back and forth three or four times, keeping it closed, carefully allow the excess of carbon bisulphide to leak out at the place where you hold the glass cover on the bottle, and then, while quickly removing the cover, approach the mouth of the bottle to a gas flame. (Pages 191 and 192).

55. PREPARATION OF NITROGEN PEROXIDE FROM NITRIC OXIDE:—The apparatus is shown by Fig 38, Page 195. Fill a glass tube, of 500 *c. c.* capacity, tubulated at one side and having a long neck, with nitric oxide, invert the flask over a basin of water so that its mouth is under the liquid, connect the tube which is fitted to the side tubulure with an oxygen gasometer (Note 14,) and, by opening the wire pinch cock which closes the rubber tube, admit a little oxygen. Brown fumes of nitrogen peroxide will at once appear; the latter gas is, however, rapidly absorbed by the water in the neck of the flask, the following reaction taking place:—

$$3\ NO_2 + H_2O = 2\ HNO_3 + NO;\ \text{(see Page 193).}$$

After the gas in the glass globe has become colorless, owing to the disappearance of the peroxide and the regeneration of a portion of the nitric oxide, add a little more oxygen, wait for the absorption of the brown fumes again and repeat the experiment until all of the nitric oxide has been used up, the water from the trough will then have completely filled the globe*.

The preparation of nitrogen peroxide by heating lead nitrate:—The apparatus is the same as that used for the preparation of oxygen by heating mecuric oxide (Note 1, Fig 1,) *excepting* that the gas must be collected by displacement of air, and not over water. Fill the hard glass tube ¼ full of a mixture of equal parts of sand and lead nitrate, (the latter ground fine in a mortar), pound the side of the tube sharply on the desk so as to form a canal for the escape of the gas (Note 3) and heat in the combustion furnace, taking care to decompose the lead nitrate at the rear end of the tube first, and when this has yielded all of the gas which it is capable of doing, advancing the flame gradually toward the mouth of the tube. By passing the nitrogen peroxide through the apparatus used in condensing sulphur dioxide (Note 43, Fig 30), itcan be obtained as a straw colored liquid; nitrogen trioxide can be liquified by the same means, the fluid is indigo blue in color; prepare the trioxide by heating a mixture of ordinary nitric acid and a little arsenious oxide* in the apparatus which you used for the preparation of sulphur dioxide, after removing the wash bottle and replacing the latter by the gas condensing apparatus, which is well cooled by means of pounded ice and salt.

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*Of course, if a globe which is tubulated is not at hand, an ordinary flask can be used, the oxygen can then be run in under the water by using a bent delivery tube.

56. THE PREPARATION OF NITRIC ANHYDRIDE:—The preparation of this substance is not infrequently attended with danger, the reaction leading to its formation is therefore scarcely to be attempted either in the laboratory or in the lecture room. Place concentrated nitric acid in a tubulated retort of about 500 *c. c.* capacity, and then gradually add phosphoric anhydride until the mixture of that solid with the nitric acid has formed a jelly-like mass, cool the retort during this operation so that the temperature never exceeds 0°, now heat *very* gently on the water bath, never allowing the temperature to exceed 60°, distill the liquid which passes off into a receiver, (arranged as in the preparation of bromine, Fig 22), which is kept cool by means of ice and salt; the nitric anhydride will then solidfy. *Do not keep nitric anhydride for any length of time!*

57. THE PREPARATION OF NITRIC ACID:—*By passing electric sparks through moist air.* Take a eudiometer tube (Fig 13, Note 20) stopper it with a rubber stopper, connect its platinum wires with a battery and induction coil and allow electric sparks to pass through for about an hour, the tube will then be seen to be filled with brown fumes if it is held against a white background, and a little blue litmus solution introduced into the tube will be turned red.†

58. THE SAME:—*By heating sodium nitrate and sulphuric acid.* The apparatus to be used is shown by Fig 39, Page 197. It is identical with that employed for the preparation of bromine (Fig 22) excepting that a drop funnel is fitted into the tubulure of the retort by means of a rubber stopper.‡ In the retort place 50 grams of potassium nitrate, make all connections and then add 50 grams of concentrated sulphuric acid through the drop funnel, warm gently until drops of liquid begin to pass over and then endeavor to keep the retort at about the temperature of distillation. After a time a crystalline remainder will form in the flask, wash this out, evaporate in an open dish and investigate the nature of the crystals by heating in a test tube, if they consist of the primary sulphate they will separate sulphuric acid on heating; repeat the experiment, using 25 grams of sulphuric acid to 50 grams of potassium nitrate, heat until no more nitric acid passes off and then, after cooling and recrystallizing the remainder, test as you did the primary sulphate (the secondary sulphate will not liberate sulphuric acid on heating in a test tube).

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* If you have none but powdered arsenic trioxide be very careful to add it very gradually to the nitric acid, and heat very gently, the reduction of the nitric acid is apt to become quite violent; if the porcelain-like variety of arsenious oxide is at hand, it is much better to use the latter form.

† Be careful to have the blue litmus solution as nearly neutral as possible and be sure to add no more than one or two drops.

‡ Nitric acid attacks rubber; it is therefore essential to have some *high melting* paraffine in the laboratory, melt a little of this and coat the rubber stopper by dipping it into the liquid, unless the temperature of any reaction becomes high enough to melt the paraffine, the latter will afford a perfect protection of the rubber.

59. EXPERIMENTS WITH NITRIC ACID:—Make a solution of indigo by dissolving a little indigo in concentrated sulphuric acid, warming slightly and then diluting with water; to this solution add nitric acid until it is bleached; take a piece of white silk ribbon and dip it into tolerably concentrated nitric acid, wash with clean water and put aside, after a time examine its color and texture. *Prepare fuming nitric acid* by placing 100 grams of ordinary nitric acid in the apparatus used for preparing bromine (Fig 22) slowly adding 50 grams of concentrated sulphuric acid through the drop funnel (Fig 39) and gently distilling; by this means the nitric acid is deprived of nearly all water with which it was mixed; now, clean the retort, put the *distillate* back into it and then add a few pieces of starch, connect the apparatus and slowly distill again, the starch will generate lower oxides of nitrogen (N_2O_3 and NO_2) while it is itself being oxidized, and these lower oxides will be disolved by the nitric acid in the receiver; fuming nitric acid is therefore nitric acid which contains lower oxides of nitrogen (see Page 196, paragraph 2). Place some of the fuming nitric acid in a test tube, as is shown by Fig 40, place the test tube inside of a beaker, in order to render an accidental cracking harmless, warm the nitric acid slightly and then drop a red hot piece of charcoal, which is cut the size of a pea, into the acid; (perform this experiment under the hood!). Try the solubility of various metals, (iron, zinc, copper, platinum,) in nitric acid, and note the gases which pass off. Take some pieces of zinc and dissolve them in very dilute, cold nitric acid; evaporate the remainder to dryness and then see if you can discover the presence of an ammonium salt (Note 49), do the same with a piece of magnesium, (Page 189, paragraph 2). Prepare *aqua regia* by mixing one part of nitric acid with three parts of hydrochloric acid, allow to stand and notice if the odor of chlorine is perceptible; dissolve a small piece of platinum in aqua regia. Heat a solution of ferrous sulphate with nitric acid, add a solution of potassium hydroxide *before* the addition, note the appearance of the precipitate; add the same solution *after* the heating and note the appearance of the precipitate. (*Ferrous* hydroxide is precipicated in the first case, *ferric* hydroxide in the second; nitric acid oxidizes *ous* compounds to *ic* compounds, [prove this also by adding the acid to a solution of sulphur dioxide in water.])

THE DECOMPOSITION OF THE NITRATES:—The decomposition of the nitrate of a heavy metal was illustrated in Note 55. *The nitrates of the alkalis* decompose into the *nitrite* and oxygen when heated. Take some potassium nitrate, place in a hard glass test tube and heat for some time to a bright red heat; bubbles of oxygen will pass off. Allow the test tube to cool, dissolve the remainder in water, add a little iodide of potassium solution mixed with starch paste (Note 22), and then a drop of sulphuric acid, iodine will at once be liberated. Do the same with some pure potassium nitrate dissolved in water and note the difference. (*Nitrous* acid at once liberates iodine from iodide of potassium because it is a very quick oxidizer, just as ozone and hydrogen peroxide are [page 50]; *nitric* acid liberates iodine only after a considerable interval of time).

60. THE PREPARATION OF RED PHOSPHORUS:—Take a piece of hard glass tubing, seal one end, place a piece of phosphorus the size of a pea into the tube and seal the other end by heating in a glass-blower's flame and allowing the sides to fall together,* place the tube upright in an

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*Substances frequently must be heated in sealed tubes. The end which is closed before filling the tube should be round, like the bottom of a test tube, and as thick as the walls of the glass tube. After the substance to be heated is added, the iron crucible of its own length and then fill the crucible with sand. Heat by means of a triple burner. By this method the glass tube will be hot below and tolerably cool above. At some point in its length the proper temperature of 300° will be reached: red phosphorus will deposit at that place. (Be sure to perform this experiment under a hood so that if the tube should explode the flying glass can do no damage.) *Never* handle the glass tube unless it is cold. *Open the tube* by wrapping a towel around it and exposing the tip of the long, sealed end to the flame; after a little air has been admitted in this way, you can break open the tube. *Never* attempt to *break open* a sealed glass tube unless you have taken this precaution.

The low kindling temperature of ordinary phosphorus can be shown by dissolving a little in carbon bisulphide and then pouring a few drops of this solution on a piece of filter paper. After the carbon bisulphide has evaporated, the finely divided phosphorus which remains on the filter paper will take fire spontaneously. (Throw the solution of phosphorus in carbon bisulphide down the sink as soon as you are through with it and then wash the test tube. Be careful while handling phosphorus.)

61. THE PREPARATION OF PHOSPHINE:—The apparatus is shown by Fig. 41. The small generating flask (100 *c.c.*) is fitted with a double bored rubber stopper, a delivery tube *b* and a tube *a* which connects with a hydrogen generator. In the generating flask place a solution of 20 grams of potassium hydroxide in 40 c.c. of water and two pieces of yellow phosphorus as large as a bean; now pass a current of hydrogen through the flask until all of the air is expelled and then heat the generating flask in a sand bath.* Phosphine will pass off and will take fire spontaneously when it reaches the air; demonstrate this by placing the end of your delivery tube under water before beginning the experiment; the individual bubbles will then rise to the surface and burn. *A simpler and better way of preparing phosphine* is to place a piece of calcium phosphide in a basin of dilute hydrochloric acid; bubbles of phosphine will at once pass off and take fire spontaneously. The gas can be collected in a test tube filled with water and inverted over the piece of calcium phosphide. Phosphine which is not spontaneously combustible can be prepared by passing the gas, generated by either of the above methods, through the apparatus used to condense sulphur dioxide (note 43); the liquid phosphine which is spontaneously combustible will then be condensed, while the gaseous phosphine will pass on.

62. THE PREPARATION OF PHOSPHORUS PENTOXIDE:—Place a piece of phosphorus on a porcelain plate, ignite it and cover with a glass bell; phosphorus will collect on the walls of the latter and on the plate. Dissolve some of the pentoxide in water and test the solution with blue litmus; expose some of the pentoxide to the air; to the solution of phosphoric anhydride add silver nitrate; boil another portion of the solution for some time, nearly neutralize with ammonia and then add silver nitrate. Take some secondary sodium phosphate (ordinary sodium phosphate) and heat a little of the salt in a hard glass test tube until water of crystallization is driven off; now heat more strongly (formation of pyrophosphate). To a solution of secondary sodium phosphate add a solution of calcium chloride and then perform the experiments suggested by the text on page 220. Take a little sodium-

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other end of the tube is sealed to a long point, not by heating the glass and *drawing out*, but by heating and allowing the sides to fall together, so that the sealed point is as thick as the rest of the tube. This operation requires considerable practice.

* A shallow iron dish containing sand.

ammonium hydrogen phosphate and heat in a hard glass test tube (notice the odor!); finally heat until the substance forms a transparent glass; place some of this transparent glass on the end of a platinum wire and heat with a little cobalt nitrate, manganese chloride, ferric chloride: using a fresh drop of fused sodium metaphosphate and a clean wire for each one of the salts.

Phosphorus trichloride, when dissolved in water produces *phosphorous* acid. Place a few drops of phosphorus trichloride in a test tube, add water and notice how the oily liquid dissolves; test the solution by means of blue litmus paper; evaporate the solution to dryness on a water bath until all of the hydrochloric acid has passed off, and then add an alcoholic solution of iodine (page 216, paragraph 2, *c.*).

Phosphorus pentachloride, when dissolved in water produces *phosphoric* acid, take a little of the pentachloride on a spatula and add it to water in a test tube. The reaction will take place at once, with a hissing noise; the solution of phosphoric acid will not reduce iodine to hydroiodic acid as the solution of phosphorous acid does.

63. MARSH'S TEST FOR ARSENIC:—The accurate details of this method belong in works especially devoted to analytic chemistry. Take your hydrogen generating flask, (note 12, Fig. 7) attach a U shaped drying tube (Fig. 14) to this and connect the latter by means of a piece of rubber tube (which is cut as short as possible) with a hard glass tube which has been drawn to a point and which is constricted at two places by being drawn out in the flame of a blast lamp.

Fill the U shaped tube one-half with small pieces of potassium hydroxide for the purpose of removing acids from the gases which pass through and one-half with granulated calcium chloride, attach the U tube with the potassium hydroxide side toward the generating flask.

Place 20 grams of pure zinc in your generating flask, add dilute sulphuric acid and allow a brisk current of hydrogen to traverse the apparatus, when all is safe; ignite the jet at the drawn out point of the hard tube, place a cold porcelain plate in the flame and see if the latter leaves a spot. Now add a solution of arsenic trioxide in hydrochloric acid to the generating flask through the thistle tube. in a few minutes arsine will be developed and the hydrogen flame will assume a violet color, with a white smoke; now heat the hard glass tube at a point just *before* one of the constrictions, amorphous arsenic will be deposited on the cold portions of the tube in the form of a mirror; *this mirror is volatile and can be driven from place to place along the tube by heating it with a Bunsen burner;* hold a cold porcelain plate in the flame at the tip of the hard glass tube, this will cool the escaping gases to a point below the kindling temperature of arsenic, the latter element will therefore be deposited on the plate as a black spot. This spot, when touched with a drop of sodium hypochlorite solution on the end of a glass rod, will be instantly dissolved ($3\,NaOCl + 2\,As = As_2O_3 + 3\,NaCl$); when touched with nitric acid it is dissolved, owing to oxidation and solution of the arsenious oxide formed. Arsine, when passed into a solution of silver nitrate, precipitates metallic silver and forms arsenic trioxide. This reaction can be obtained by extinguishing the flame at the tip of the hard glass tube and passing the mixture of gases which are being generated into a test tube containing silver nitrate solution, black, metallic silver will be precipitated; filter this off and add ammonia to the clear filtrate, until neutral, yellow arsenite of silver will be precipitated. If the gas which is passing from the generator is *stibine* and not arsine the mirror spots on the tube will have a greyish and more metallic appearance, will form nearer to the flame and will be very nearly not-volatile. The spot on the porcelain mirror will not disappear on addition of sodium hypochlorite, it will turn white on addition of nitric acid, because the oxide of antimony is insoluble in that substance; if *stibine* is passed into a solution of silver nitrate, black silver antimonide, Sb Ag_3 is precipitated, if this precipitate is treated with tartaric acid, then the antimony will be dissolved and its presence can subsequently be readily proved by precipitating antimony sulphide by means of sulphuretted hydrogen. For further directions consult some work on analytical chemistry. (See page 227). (All work with arsine or stibine must be done under the hood!)

64. A QUICK METHOD FOR DETECTING ARSENIC:—Draw a piece of hard glass tube to a point as is shown in Fig. 42, place a little arsenious oxide or a small particle of the substance which you suspect to be arsenious oxide in the tip, above this place a small piece of charcoal, heat the tube at the spot where the coal has lodged until the latter is red hot and then, gradually, draw the tube through the flame until the arsenic trioxide is heated, the latter will sublime and will, in passing over the hot charcoal, be reduced to metallic arsenic, the latter forming a mirror similar to that observed in Marsh's test.

The experiments which can be performed with the oxides and sulphides of arsenic will suggest themselves during the study of chapters 32 and 33.

65. STIBINE:—The preparation of stibine is exactly like that of arsine so that the pupil can follow the directions given in note 63, excepting that he must substitute a hydrochloric acid solution of antimony trioxide for that of arsenious oxide. The distinctions existing between the spot produced on a cold plate by burning arsine and that produced by stibine are given in the last part of note 63, the experiments showing such distinction should be followed out. As antimony and arsenic are elements which are commonly met with in analytical work and as their reactions are fully described in all of the directions for qualitative analysis which are published, it is scarcely necessary to enter into a more detailed discussion of experiments to be performed with antimony at this place. By following the text the teacher can easily select expertiments which need no detailed description (pages 242, 343 and Chapter 35). The same is true as regards bismuth.

66. DESTRUCTIVE DISTILLATION OF COAL AND WOOD:—Unless a laboratory is especially well appointed and unless the pupil has plenty of time at his disposal, it will not be possible to carry out the dry distillation of bituminous coal or of wood, when such work is attempted it belongs, more properly, into a course on organic chemistry. The pupil should, however, place a small piece of wood in a hard glass test tube and heat, endeavoring as much as possible, to ascertain the nature of the products evolved; he should also see if the gases which pass off will burn. The same experiments should be performed with a piece of bituminous coal.

67. THE ABSORPTION OF COLORING MATTER BY CHARCOAL:—Prepare a solution of indigo (note 59), place in a 300 c. c. flask and warm, after adding two tablespoonfuls of animal charcoal;* filter and if the solution is not colorless, repeat the operation. Do the same with a solution of iodine in iodide of potassium. The absorption of gases by charcoal was given in note 49.

69. THE FLAME:—The fact that the center of a flame is cold, while the outer zone is hot can be demonstrated by turning the flame of a Bunsen burner down, shutting off the air supply so that the flame becomes luminous and then quickly placing a sheet of filter paper

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* Animal charcoal can be obtained at any chemical supply house.

upon it, so that about one-half of the flame is below the surface of the paper (Fig. 43); as soon as the brown, burnt circle appears on the upper side of the paper, withdraw the latter quickly. A more striking illustration of this can be brought about by the apparatus shown by Fig. 46, page 273. This consists of an ordinary argand lamp-chimney which is closed at the bottom by a cork. through a hole in the center of which a glass tube admits illuminating gas. The upper part of the chimney is covered with a wire gauze; a little gun-powder is placed in the center of this gauze and then the gas is turned on, the jet afterward being lighted by bringing a lighted taper toward the chimney from *above downward.* The gunpowder will then be surrounded by a circle of flame, but will not explode.

Diluting illuminating gas with a non-combustible gas renders the flame not-luminous. Arrange an apparatus as is shown by Fig. 44. Attach one arm of the T-shaped glass tube to a tap of illuminating gas and attach the other to an apparatus generating dry carbon dioxide; the remaining arm of the T tube is fitted with a brass pipe which can be heated by a Bunsen burner. Turn off the supply of carbon dioxide by the pinch cock, turn on the gas and light the burner, the flame will of course be luminous. Now, turn on the carbon dioxide so that the latter gas mingles with and dilutes the illuminating gas; the flame will at once become larger and *not-luminous.* However, if the brass exit tube which serves as a burner is heated to a point at which the decomposition of ethylene into methane and carbon takes place, the flame will once more be rendered luminous, although still diluted by carbon dioxide.

A flame can be extinguished by cooling below the kindling temperature:—Light a Bunsen burner and then place a piece of copper wire gauze upon the flame so that the latter will about be bisected; the flame will continue to burn beneath the gauze, but above the latter, because the wire conducts the heat away too rapidly, no flame will be seen. The reverse of this experiment (Fig. 45) is shown by placing the gauze above an unlighted burner, turning on the gas and then lighting *above* the gauze; the flame will then not form below.

To show that oxygen will burn in illuminating gas:— Construct an apparatus as shown by Fig. 47. The tube *B* is connected with an illuminating gas tap, the gas turned on and allowed to run until all air is expelled from the glass bulb; now light the gas at the top, the double bored stopper containing tubes *A* and *C* being removed for the purpose. Attach *A* to a gasometer which will furnish oxygen, turn on a slow stream of that gas and then bring the stopper which holds *A* and *C* back into position. As the current of oxygen comes in contact with the burning gas escaping from the bulb it will be ignited and will continue to burn in the illuminating gas.

70. THE PREPARATION OF CARBON MONOXIDE BY PASSING STEAM OVER RED HOT CHARCOAL:—Take an iron gas pipe 700^{mm} in length; attach one end of it, by means of a rubber stopper, to a flask of 300^{cc} capacity which is so arranged on a retort stand that you can boil water in it and that the steam must pass through the iron tube. Connect the other end of this iron tube with a safety bottle (Note 1) and put a delivery tube, bent so that it will open under the water in your pneumatic trough, into the latter; place the iron tube into a combustion furnace (Fig. 1, note 1), having previously filled the tube with pieces of charcoal which are broken to the size of a pea, heat to a red heat and then pass steam over the charcoal. After all of the air has been expelled from the apparatus by means of the current of steam, collect the escaping gas over the pneumatic trough by displacement of water. This gas will be

carbon monoxide, as can be proven by inverting one of the cylinders filled with it and touching a lighted taper to the mouth.*

71. THE PREPARATION OF CARBON MONOXIDE FROM OXALIC ACID:—The apparatus is the same as that used for nitrous oxide (Note 52, Fig. 37). In the retort place 10 grams of crystallized oxalic acid, add 60 grams of concentrated sulphuric acid and heat until a regular evolution of gas takes place; pass this gas through a wash bottle (Fig. 8) containing a solution of potassium hydroxide (one part potassium hydroxide to two parts of water) before you collect over the pneumatic trough. By means of this wash bottle the carbon dioxide, which is generated simultaneously with the carbon monoxide, is absorbed (it forms potassium carbonate) while pure carbon monoxide is collected; the latter gas will burn with a pale blue flame.

72. THE PREPARATION OF CARBON DIOXIDE:—The apparatus is the same as that used for the preparation of hydrogen or of hydrogen sulphide (Fig. 7, note 12). Charge the generating flask with 20 grams of marble which has been broken to the size of a hickory nut, pour on 100^{cc} of hydrochloric acid, which you have diluted with an equal amount of water, and pass the gas which is generated through a wash bottle containing water (if dry carbon dioxide is required, pass the gas through a second bottle containing sulphuric acid); collect the carbon dioxide by displacement of the air as you did chlorine and hydrobromic acid.

Take a number of other carbonates (sodium carbonate, potassium carbonate, barium carbonate, etc.), place a little of each in test tubes and add hydrochloric acid to each test tube; ascertain if carbon dioxide is given off.

73. EXPERIMENTS WITH CARBON DIOXIDE:—Fill 5 or 6 cylinders with carbon dioxide. Construct an apparatus such as is shown by Fig 48: a number of small candles are placed on wires which are attached in an upright position to a larger wire which is bent in the form of a flight of steps; light all of the candles, place them in a beaker glass and pass carbon dioxide into the latter by means of a tube extending to the bottom; the lights will be extinguished successively from *below upward*, this experiment will also demonstrate the fact that carbon dioxide neither burns nor supports combustion. Pass some carbon dioxide from your generator into a solution of barium hydroxide and into one of calcium hydroxide; filter the precipitate formed in each case, wash them from the filter papers into test tubes and add hydrochloric acid, prove that carbon dioxide is passing off by holding a glass rod which has been dipped into lime water (a solution of calcium hydroxide) just within the mouths of the test tubes, if carbon dioxide is being generated, the lime water will become turbid. Pass carbon dioxide into a concentrated solution of potassium hydroxide and into one of sodium hydroxide, take a little of the solutions so formed and add hydrochloric acid to them; prove that carbon dioxide passes off. Pass carbon dioxide into a solution of lime water until the precipitate which at first forms is redissolved, (formation of the primary carbonate) and then boil the solution; add hydrochloric acid to the solution before it is boiled and to the precipitate which is formed by boiling and see if carbon dioxide is given off in each case.

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* In using the combustion furnace for this experiment, take care that the iron tube is sufficiently long to extend some little distance beyond either end of the furnace, otherwise the rubber stoppers will become too hot and will melt; you should feel of the stoppers from time to time and if there is danger of their fusing, cool them by pouring on water from time to time.

74. THE ETCHING OF GLASS BY MEANS OF HYDROFLUORIC ACID:—Take a shallow lead dish 3 inches long, 2 inches wide and 1 inch deep, put about 10 grams of powdered calcium fluoride into this and cover the fluoride with sulphuric acid; prepare a piece of window glass by dipping the same with melted paraffine, * allowing the latter to cool and etching some figures by scratching away the paraffine coating with the point of a knife, place this prepared glass over the lead dish in the form of a cover, put the whole into a warm place under the hood and allow to stand for 6 or 8 hours, the glass will then be etched where the paraffine was scratched away.

Preparation of silicon tetrafluoride and of fluosilicic acid:—Take a flask of 300 *c. c.* capacity, put into this 50 grams of quartz sand mixed with 50 grams of powdered calcium fluoride; fit a single bored rubber stopper to the flask, and in this rubber stopper place a glass delivery tube which is bent with two right angles; the end of this delivery tube will then point downward; to this end attach a funnel by means of the stem, in such a manner that the escaping gas must pass through the funnel, and place a beaker of water under the latter so that its rim just touches the surface of the water. Pour 100 grams of concentrated sulphuric acid on the mixture of sand and calcium fluoride in the generating flask, connect the apparatus and warm gently; silicon tetrafluoride will pass off and will come in contact with the water in the beaker, by this means, fluosilicic acid will be formed. The solution of the latter will be filled with flakes of silicic acid so that, if the delivery tube had not been widened by the funnel, it would soon have become clogged and an accident would have followed. Filter the fluosilicic acid from the precipitated silicic acid and test the reaction of the solution toward litmus; add just enough potassium hydroxide solution to neutralize the fluosilicic acid and then allow to stand, insoluble potassium fluosilicate will separate.

The elements which follow silicon in the text are nearly all of a metallic nature, and none of the experiments which will fix their character in the mind of the pupil will present any practical difficulty. It is better, therefore, for the teacher to select such experiments as he deems proper from the text, indeed, it often seems advisable to study some of the chemical relations of the metals in the laboratory by the methods of qualitative analysis, while, at the same time, becoming familiar with the more general aspect of the chemistry of those elements by following the text book on general chemistry; the small manuals containing directions for qualitative analysis are, however, so numerous that it seems unnecessary to add a list of experiments, which practically cover the same ground, to a text book of general chemistry.

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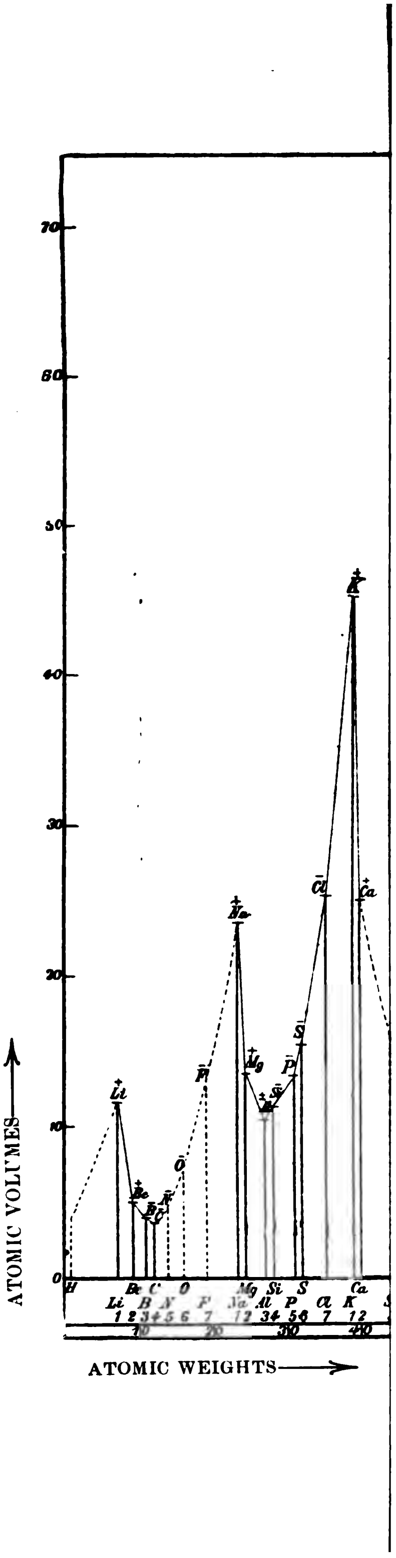
* Use so-called high melting paraffine.


ATOMIC VOLUMES
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Mg
Al
Si
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ATOMIC WEIGHTS

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